Mixed Matrix Composite Membranes Containing POSS Molecules for Carbon Dioxide Removal Application

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ABSTRACT

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for Carbon Removal Application

Eki Listya Rini

CO_2 removal by membrane processes is considerably potential for several applications such as natural gas and synthesis gas purification, enhanced oil recovery application, and carbon dioxide capture in combat against global warming. Dense polymeric membranes are commonly utilized for these type of gas separation applications. Nevertheless, the intrinsic properties of dense polymeric membranes, which commonly characterize by the low gas permeability versus high gas selectivity trade–off or vice versa, is less desirable. In order to meet the increased demand of CO_2 removal, a strategy to improve the gas separation performance of a polymeric membrane is investigated in this study. With this regard, mixed matrix membranes in which inorganic non porous fillers are incorporated into a polymeric matrix were prepared to achieve the aforementioned objective. The mixed matrix membranes were prepared from Pebax® block copolymers and PEG POSS® molecules. These hybrid membranes were formed as both dense and multilayer composite membranes. The dense transparent membranes with well–dispersed fillers could be obtained by variation of the solvent mixture. The DSC analyses showed that incorporation of PEG POSS® into Pebax® matrix altered the thermal properties of the matrix. The multilayer composite membranes were then prepared from a PTMSP gutter layer deposited on a PAN porous support and an adjacent hybrid Pebax®/PEG POSS® as the top layer. These hybrid multilayer composite membranes exhibited an enhanced CO_2 selectiv-

ity by a factor of two relative to the pure Pebax®. In these hybrid systems, the CO_2 separation was presumably enhanced by the high ether oxides content from PEG POSS® that has high affinities for CO_2. For particular composition of Pebax® and PEG POSS® concentrations, the PTMSP gutter layer harnessed the CO_2 selectivity without losing the CO_2 permeation rate. At the same time, these membrane, however, suffered severe adhesion between the gutter layer and the top selective layer, and this problem led to the decreased separation performance. This study showed that the hybrid multilayer composite membrane could be considerably attractive for CO_2 removal application if the characteristics of each layer were appropriately matched and optimized.

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TABLE OF CONTENTS

List of Illustrations

List of Tables

Chapter I

Introduction

During the recent years, there is an increasing interest in carbon dioxide separation from mixtures with light gases using membrane processes [6]. In natural gas applications, the removal of CO_2 is required in order to meet pipeline specifications; since the presence of CO_2 beyond a certain limit (i.e., 2 vol% or less in U.S.A) reduces the heating value of natural gas, may form blocks of dry ice at low temperatures that plug the equipment, or may corrode the equipment [7]. Carbon dioxide separation from natural gas using membranes is also useful for enhanced oil recovery (EOR) application; since this process needs a high CO_2 concentration at high pressures [7]. Likewise, the hydrogen produced via steam reforming of natural gas should also be purified from CO_2 before its usage in hydrogen refineries or as an energy source [7]. Another attractive application is CO_2 capture from fossil fuels combustion and industrial processes. The increase in CO_2 emission in the atmosphere is one of the recent major environmental issues due to its contribution to the global warming [8]. The aforementioned applications are in huge–scaled [9], thereby the demand for more energy–efficient and cost–effective CO_2 removal processes would likely increase in the coming years.

Currently, a hybrid configuration of membrane and traditional technology (i.e., absorption or pressure swing adsorption) is an attractive option for carbon removal applications [10]. Membrane processes, however, can compete effectively with the other technologies when membranes are used in small or medium–scaled separation process and the requirements for the permeates are not very rigorous [11]. Membrane processes offer low capital investment, low operating cost, and ease of opera-

tion compared to the other traditional technologies [11].

In gas separation applications, polymers dominate the membrane materials because they are easy to process and have a sufficient gas selectivity [12]. In the last decades, the state of the art of novel polymeric membranes has been focusing on the improvement of their selectivity toward a specific gas [11]. This approach can be done either by modification of polymer chemical structure or by post–treatment of polymeric membranes [11]. Nevertheless, the improvement of polymeric membrane selectivity is often coupled with reduced gas permeability, and vice versa [13]. Therefore, the strategies to enhance the gas selectivity of a polymeric membrane while keeping the gas permeability nearly intact or even increased need to be further explored.

I.1 Objective

In accordance with the preceding statement, a strategy to enhance the gas separation properties of a polymeric membrane for carbon removal application is developed in this thesis.

Koros suggested a mixed matrix system, blends of molecular sieving material in a polymer matrix, in order to fabricate membranes that exhibit high gas separation performance [14]. Hybrid organic–inorganic systems are found useful to improve the gas separation performance of polymers relative to the pure ones. In the initial stage of development, mixed matrix systems were fabricated using the micro–sized fillers. Recently, the development of mixed matrix system has advanced rapidly to the nanometric or molecular level. Some of the current nanocomposite membranes exhibited a high gas separation performance coupled with a high gas productivity [15]. In addition to that, mixed matrix solution can be cast in a porous polymeric support forming a composite membrane construction by using the current membrane formation technology [16]. A composite membrane is constructed from one

or more thin dense polymeric layers coated on top of a support layer. The thin dense layer functions as selective region where the separation occurs, whereas the support provides a mechanical strength for the top layer. For practical sense, this type of membrane provides benefit since the support are readily in low cost, so that balancing another expense required for the mixed matrix selective layer. The economical factor is important to allow a newly–developed membrane for successful implementation.

Firstly, the dispersed fillers should be carefully matched to the polymer matrix, as the intrinsic gas transport properties of both materials will control the resultant gas transport properties [16]. In accordance with the material selection, block copolymers, which contain PEO segments, have been extensively studied for carbon removal applications. It was shown that ether oxides in PEO block have a specific affinity for CO_2 [17, 18] and thus enhances the CO_2 selectivity over other gases. Poly(amide–b–ethylene oxide), also known with commercial name Pebax®, is one of the examples. Pebax® is a potential candidate for CO_2–selective membrane material [19]. This block copolymer has a high CO_2 selectivity over non–polar gases, for example, H_2, N_2, and CH_4 [20]. Hybrid polyhedral oligomeric silsesquioxanes (POSS) molecules have also been investigated for nanofillers in preparation of novel nanocomposite membranes. Li et al. [21] reviewed that mechanical, dynamic, or gas transport properties were enhanced by incorporating POSS molecules into a polymer matrix. Therefore, a mixed matrix composite membrane will be prepared by combining both unique properties of Pebax® block copolymer and POSS molecules for carbon removal application. In this work, the octa polyethylene glycol POSS, namely PEG POSS®, is chosen as the filler particles. There are some considerations in accordance with the filler selection: first, PEG POSS® having a PEG groups, which is rich ether oxides, is expectedly able to improve the CO_2 selectivity; second, it is also expected that the PEG POSS® particles having nanometric size will be dis-

persed and distributed homogeneously in the polymer matrix relative to the other micrometric–sized fillers.

Second, the preparation of composite membrane should also be taken into account. The preparation involves the production of porous support and the casting of the selective layer that can be done individually. One key issue in composite membrane preparation is to control the surface pores size of a support layer in order to harness the separation property of a selective layer [10]. It is important that the diameter of the surface pores of a support layer is less than the hydrodynamic radius of the polymeric coils. Unless, the polymer coils will penetrate into the support pores and thus reducing the gas separation performance [10]. There are some useful strategies to avoid this issue: first, by filling the pores with an appropriate non–solvents mixture prior to the casting of a selective layer; second, by application of a thin pre–coating layer from a highly–permeable and low–selective polymer above the support layer, a so–called gutter layer [10]. In this work, the appropriate strategy for a composite membrane of interest will also be further investigated. Poly(1–trimethylsilyl–1–propyne) (PTMSP) will be used as material for a gutter layer. PTMSP has a very high permeability [22], and thereby it meets the requirement for a gutter layer. For another strategy, the support pores first will be filled by ethanol/water prior to the casting of the selective layer. A mixture of ethanol/water can be applied onto the support's surface since it does not dissolve the polyacrylonitrile (PAN) support [23]. By implementing these approaches, it is expected that the gas separation performance of the composite membranes will be enhanced.

I.2 Problem Definition

Based on the objective above, the following question arises: *How is the gas separation property of Pebax®/PEG POSS® mixed matrix composite membranes for carbon removal applica-*

tion?

Accordingly, this question evolves into several questions as follows:

1. What is the effect of the PEG POSS® incorporation on the thermal property of Pebax® copolymer?

2. What is the gas separation property of composite membranes prepared from PAN (support layer) and Pebax® (selective layer)?

3. What is the effect of pre–coating of non–solvents mixture (ethanol/water) onto the PAN (support layer) on the gas separation property of the composite membranes?

4. What is the effect of PTMSP (gutter layer) on the gas separation property of the composite membranes?

5. What is the gas separation property of mixed matrix composite membranes prepared from PAN (support layer) and Pebax®/PEG POSS® (selective layer)?

As the problems have been defined above, these following approaches are used in order to solve those aforementioned problems:

1. To investigate the gas separation property, membranes are characterized using gas flux measurement.

2. To investigate the thermal property, membranes are characterized using differential scanning calorimetry (DSC).

3. To investigate the cross–sectional morphology, membranes are characterized using scanning electron microscopy (SEM).

I.3 Report Structure

This thesis is written with the following structure:

Chapter One presents the background and objective, as well as the defined problems for the present work.

Chapter Two discusses the fundamentals of gas transport properties and composite membranes. The state of the art of nanocomposite membranes for carbon removal applications is briefly discussed in this chapter.

Chapter Three details the experimental methods carried out in this work, that is including the materials, sample preparation, and membrane characterization.

Chapter Four presents the obtained results. Furthermore, discussion of the results is also presented.

Chapter Five summarizes the report with a conclusion.

Chapter II

Polymer-based Membranes for Carbon Removal Applications

II.1 Fundamentals

II.1.1 Gas transport properties of polymer

The ability of polymeric materials to permeate gas molecules and to separate gas mixtures had been investigated over a century ago [24]. In 1866, Graham pioneered one of the early studies in permeation process and gas separation using membrane [24]. Graham postulated that the permeation of gases through a dense membrane occurred by the solution–diffusion mechanism [25]. The gas molecules firstly dissolve in the high–pressure side of the membrane, diffuse across a concentration gradient to the low–pressure side of the membrane, where the gas molecules finally desorb. This mechanism can be applied with the assumptions that the diffusion is the rate–limiting process, and the gas phase in either sides of the membrane achieves equilibrium with the gas in membrane interface [26, 27].

Later, von Wroblewski developed a mathematical analysis of the permeation process that integrated the observations from the earlier studies and introduced a permeability coefficient [25]. The gas permeability, P, across a membrane with thickness l in a steady–state condition is given by the following expression

$$P = \frac{N}{(p_2 - p_1)/l} = \frac{N}{\Delta p/l} \tag{II.1}$$

where N is the flux of gas permeates the membrane (in $m^3(STP)/(m^2s)$), p_2 and p_1 are the high–pressure side and low–pressure side, respectively (in kPa), and l is the membrane thickness (in m).

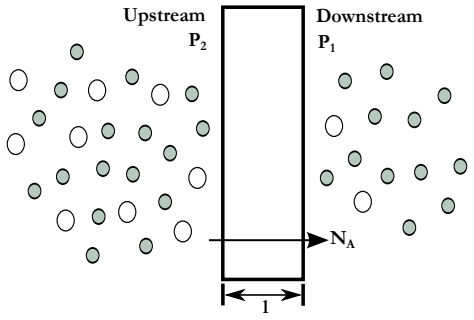


Figure II.1: Illustration of permeation process across a membrane

Furthermore, von Wroblewski showed that if the gas diffusivity obeys Fick′s law, the permeability is equal to the penetrant diffusivity times the penetrant solubility [25]

$$P = \frac{N}{\Delta p/l} = -\frac{D(\ dC/\ dx)}{\Delta p/l} = \frac{D(C_2 - C_1)}{\Delta p/l} = DS \tag{II.2}$$

where D is the effective diffusivity coefficient (in m^2/s), and S is the apparent solubility coefficient that is the ratio of the penetrant concentration in the high–pressure side of the membrane or the sorption isotherm (in $m^3(STP)/m^3polymer$), C, to the pressure of this side, p. S is called as the apparent solubility coefficient. The equation II.2 presents the analytical expression of the solution–diffusion model.

The membrane selectivity for gas A relative to gas B is given by the following expression [11]

$$\alpha_{A/B} = \left(\frac{P_A}{P_B}\right)\left(\frac{\Delta p_A/x_A}{\Delta p_B/x_B}\right) \tag{II.3}$$

where P_i is the permeability of pure gas i, Δp_i is the partial pressure difference of gas i across the membrane, and x_i refers to the mole fraction of gas i in the gas phase in the high–pressure side of the membrane. Equation II.3 implies that the selectivity of a membrane is closely related to the intrinsic properties of the polymer,

the gas pressure, and the gas composition. If it is assumed that the pressure in the low–pressure side is very low relative to the high–pressure side, so that can be neglected, the selectivity can be further expressed as ratio of the gas permeabilities [11]

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{II.4}$$

where $\alpha_{A/B}$ is the ideal selectivity. Combining the equation II.2 and the equation II.4, the selectivity becomes [11]

$$\alpha_{A/B} = \left(\frac{D_A}{D_B}\right)\left(\frac{S_A}{S_B}\right) \tag{II.5}$$

where D_A/D_B is the diffusivity selectivity, that is the ratio of the diffusivity coefficients of both gases; and S_A/S_B is the solubility selectivity, that is the ratio of the solubility coefficients of both gases.

Gas transport and sorption of rubbery polymers

In rubbery polymers, gas transport can be described as in the ideal system where both the diffusivity and the solubility are independent of the gas concentration [28]. The sorption isotherm is linear, and the concentration of gas in the polymer is proportional to the driving force, so that the sorption obeys Henry′s Law: $C = k_D p$, where k_D is the Henry′s constant and p is the pressure of gas in the polymer interface [11]. Similarly, the gas diffusion coefficient is often constant at low penetrant concentration, thus Fick′s Law can be applied [11]. In the same condition, the gas permeability is independent of pressure, so that it can be expressed by $P = k_D D$, where D is the diffusion coefficient [11].

Gas transport and sorption of glassy polymers

Differ from rubbery polymers, glassy polymers are non-equilibrium materials, thereby their physical properties are shifting over time [29]. This phenomenon arises from

the existence of the non–equilibrium excess volume in glassy polymers [11]. This volume provides an additional sorption site that increases the gas transport and sorption in glassy polymers to the greater extent than that of equivalent rubbery polymers. To model the gas transport and sorption in glassy polymer, the dual mode model is commonly used [25]. The dual mode model assumes that there are two different environments in the non–equilibrium glassy states: the volume filled with the packed structure of polymer (dissolved mode) and the excess volume (Langmuir mode). It is also assumed that the penetrant molecules are being partitioned, and exist in equilibrium resulting from the rapid exchange between these two environments. Based on this model, the sorption isotherm in glassy polymers can be expressed as follows [11]

$$C = C_D + C_H \tag{II.6}$$

$$C = k_D p + \frac{C'_H b p}{1 + bp} \tag{II.7}$$

where C is the total penetrant concentration, C_D is the penetrant concentration in the dissolved mode, C_H is the penetrant concentration in the Langmuir mode, C'_H is the hole saturation constant or Langmuir sorption capacity, and b is the Langmuir affinity parameter. For a low–concentration penetrant in glassy polymer, however, Henry's Law is still useful to model the sorption isotherm [25].

In addition, the non–equilibrium excess volume also contributes to the gas permeability of glassy states. When the pressure in the low–pressure side can be neglected, the gas permeability can be explained by [11]

$$P = k_D D_D + \frac{C'_H b D_H}{1 + bp} \tag{II.8}$$

In this expression, D_D and D_H refer to the gas diffusivity coefficients in the dissolved mode and Langmuir mode, respectively, and p is the pressure in the high–pressure

side of the membrane.

II.1.2 Gas transport properties of hybrid organic–inorganic membranes

Mixed matrix membrane has been proposed as one of the potential routes for future membrane separation applications [30]. This membrane involves inorganic particles, either porous or nonporous particles, dispersed in a polymer matrix. The combination between the superior separation properties of inorganic filler and the flexibility of polymeric material offers potential strategy to achieve higher separation properties relative to the pure polymeric membrane. The resultant properties of mixed matrix membranes, however, depend upon the intrinsic properties of each phase. Regarding to that, the porous fillers affect the resultant mixed matrix membrane properties differently from the nonporous fillers [31]. As a result, mixed matrix membranes comprising porous filler and nonporous filler differ in their gas transport mechanisms as well as the correlations used to model the permeation on each membrane.

In ideal case, where the membrane has no defect (interface voids or rigidified polymer chain) and the separation properties of each phase are not distorted, the well–known Maxwell analysis provides a reasonable approach to predict the permeation properties in a mixed matrix membrane [30]. For nonporous fillers dispersed in a polymer matrix, this analysis is expressed as follows [1]

$$P_c = P_m \left(\frac{1 - \phi_d}{1 + 0.5\phi_d} \right) \tag{II.9}$$

where P_c is the effective permeability of the composite membrane, ϕ_d is the volume fraction of the dispersed filler particles, and P_m is the permeability of the unfilled polymer matrix.

The gas sorption in a mixed matrix membrane comprising dispersed nonporous fillers is dependent upon several factors such as the polymer–filler interaction and

the concentration of the filler particles [31]. In the situation where the fillers are nonporous and they interact favorably with polymer chains, so that the fillers are wetted by polymer chains, the sorption by the filler particles is often neglected [32] In this case, the gas sorption can be expressed as [32].

$$S = (1 - \phi_d)S_m \tag{II.10}$$

where S_m is the penetrant solubility in the polymer matrix. In the other hand, if the fillers do not fully interact with the polymer chains, the gas sorption on the fillers also contributes to the overall gas sorption in the membrane [32], that is

$$S = (1 - \phi_d)S_m + \phi_d S_d \tag{II.11}$$

where S_d is the penetrant solubility onto the surface of the nonporous fillers.

The Maxwell analysis given in equation II.9 predicts that the addition of inorganic nonporous filler into the polymer matrix reduces the gas permeability [1]. It was observed, however, there are several existing mixed matrix membranes that do not follow the Maxwell approach. This deviation showed that the Maxwell approach oversimplifies the morphology of the real polymer–inorganic systems, and it also neglects both the matrix–filler and filler–penetrant interactions [16, 1]. Due to this additional complexity, various theoretical approach have been developed to model the gas permeation in mixed matrix membranes. Hashemifard et al. [33] reviewed several models for permeation of gases in mixed matrix membranes including Maxwell model, Lewis–Nielsen model [34], Felske model [35], Maxwell model modified, and Lewis–Nielsen model modified. In this study, they compared the models with the experimental data from the other independent studies. The comparison study showed that the most accurate model for predicting permeation of gases in mixed matrix membranes among those models is the Felske model.

II.2 Reverse–Selective Nanocomposite Membranes

Membrane process has been proposed as an attractively viable route for carbon removal applications due to their energy– and cost–efficiencies [36]. Polymer–based nanocomposites, in which the nanoparticles (the size is less than 100 nm at least in one–dimension) filled in a polymer matrix, is one of the useful approaches proposed to fabricate novel membranes [37]. This strategy offers opportunities to combine two unique properties of materials, for example the high molecular sieving characteristics of nanoparticles such as zeolite and carbon nanotubes with the easy processability of polymers. Generally speaking, reverse–selective nanocomposite membranes, which preferentially permeate heavier components (i.e., CO_2) from mixtures with light gases (i.e., H_2, N_2, and CH_4), will be useful for carbon removal applications in industrial scale [38]. In most of carbon removal processes, carbon dioxide often presents in low concentrations. By removing the minor component, reverse–selective membranes will require smaller surface area and economize the capital cost. Furthermore, the lighter gas will be maintained in the high–pressure conditioned that is more advantageous for future gas processing. Merkel et al. [39] outlined the strategy to design reverse–selective membranes by using a highly free volume polymer that sieves gas molecules weakly based on differences in molecular size. In this approach, the diffusion selectivity is driven close to unity ($D_A/D_B \rightarrow 1$); so that the solubility selectivity will be enhanced ($S_A/S_B > 1$), because the more soluble gas will permeate easily. Another worthy approach is to introduce specific chemical moieties into the polymer or composite in order to promote preferential interactions with the carbon molecules thus increasing the carbon permeation through the membranes [40, 41]. In this following section, several aspects in accordance with the preparation of nanocomposite membranes for gas separation applications will be briefly discussed.

II.2.1 Preparation of nanocomposite membranes

To obtain the novel properties of nanocomposites, the processing method plays significant role since it will determine the particle size distribution, dispersion, and interfacial interaction between particle and polymer [37]. There are three common methods for preparation of nanocomposite membranes: solution blending, sol–gel, and in–situ polymerization [37, 1].

Solution blending is the simplest method to prepare nanocomposite membranes. This can be done either by addition of stipulated amount of nanoparticles into the prepared polymer solution, addition of polymer into the nanoparticles–containing solution, or mixing both of the polymer solution and solution containing nanoparticles that have been prepared individually. After that, the membranes can be obtained by solvent evaporation or precipitation. In in–situ polymerization, the filler particles are firstly added into the monomer or monomer solution, then they are polymerized to produce the membrane. Lastly, in the sol–gel method, the polymers and the nanofiller precursors are mixed in a solution; then hydrolysis and other reactions are carried out to form the dispersed phase of nanoparticles in the polymer matrix. Among those methods, the sol–gel method is most widely used in order to obtain more homogeneously dispersed phase in a membrane [42, 1].

II.2.2 Structure of nanocomposite membranes

Based on the preparation methods above, there are two types of polymer–inorganic nanocomposite membranes; first, the covalently bonded polymer–inorganic phases that is prepared by either in–situ polymerization or sol–gel methods (see figure II.2(a)), and the polymer–inorganic phases connected by hydrogen bonds or van der Waals forces prepared by solution blending (see figure II.2(b))[1].

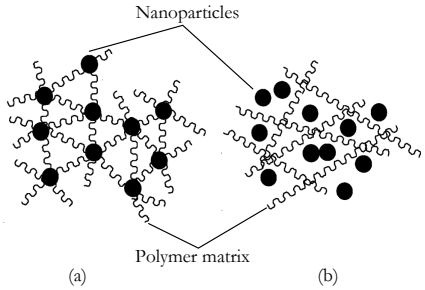


Figure II.2: Illustration of nanocomposite structures (a) covalently bonded polymer–inorganic phases (b) polymer–inorganic phases connected by hydrogen bonds or van der Waals forces ([1])

II.2.3 Gas separation performance of nanocomposite membranes

During the past few decades, various nanocomposites consisting of nonporous nanofillers and organic polymer have been investigated for separations of large organic molecules over light gases. Several representative organic/inorganic nanocomposite membranes will be presented in this section. Furthermore, a brief discussion on how the incorporation of nanofillers affecting the gas separation performance in each membrane will be also included here.

Polyimide is one of the most important polymers for gas separation membranes [12]. Because of that, polyimide/inorganic membranes have received a lot of attention in the early studies of nanocomposites development for gas separation applications. One example is the study by Kusakabe, et al. [43] that reported fabrication of a polyimide/SiO_2 hybrid membrane for CO_2 separation. Sol of polyimide/SiO_2 firstly coated on a γ–alumina–coated porous support, imidization then was carried out at 350 °C to fabricate a defect–free thin nanocomposite layer. It was shown that the incorporation of 68 wt% of silica could enhance the CO_2 permeation rate by one order of magnitude higher than the pure polyimide membrane. They also reported that the selectivity of CO_2/N_2 was about 30 at 30 °C. In this work, the contributions of polyimide-silica phases were investigated using a two–phase permeation model. The model showed that the optimum silica content in the nanocomposite was 60–70

wt% without any significant loss of selectivity relative to the neat polyimide.

Nanocomposites could also be developed from a higly free volume polymer and nonporous fillers as outlined in previous section (see section II.2). Merkel, et al. [39] investigated a nanocomposite membrane that was fabricated from combinations of a highly–free–volume poly(4–methyl–2–pentyne) (PMP) and nonporous fumed silica particles having hydrophobic trimethylsilyl surface groups. As observed by positron annihilation lifetime spectroscopy (PALS) analysis, the addition of fumed silica particles gradually increased the intrinsic free–volume element of PMP, and in turn, this enhanced the large organic molecules diffusion through the membrane. Importantly, the selectivity of large gases increased simultaneously with increased gas permeation. For example, by addition of 30 wt% fumed silica, the mixed–gas n–butane/methane selectivity was doubled and n–butane permeability was improved by a factor of 3 relative to the neat PMP at 25 °C.

Implementing the same approach, Merkel, et al. [44] also investigated the effects of fumed silica loading on gas separation performance for another highly–free–volume polymer, poly(1–trimethylsilyl–1–propyne) (PTMSP). Mixtures of PTMSP and fumed silica were prepared by solution blending method, and the dense films were obtained by solution casting. It was shown that by addition of 40 wt% fumed silica into PTMSP, the methane permeability was 180% higher than the permeability of the neat polymer. The systematic improvement of pure gas permeability in PTMSP/fumed silica nanocomposites was qualitatively similar to the aforementioned PMP/fumed silica system. As confirmed by PALS analysis, the addition of fumed silica affected the microstructure of PTMSP providing larger free volume elements available for gas transport. In contrast to PMP/fumed silica system, however, the large molecules/light gases selectivity of filled PTMSP reduced relative to the unfilled one. For example, PTMSP containing 50 wt% fumed silica had mixed–gas n–butane/methane selectivity of 64% lower than in pure PTMSP. This result ap-

peared to be associated with the PTMSP′s intrinsically microporous structure, so that when fumed silica particles were added, the pore–flow (i.e., Knudsen diffusion) transport mechanism became more pronounced than the solution-diffusion mechanism. Nevertheless, it again showed that the incorporation of nonporous nanoparticles could increase the gas permeability. In those two cases, enhancement of gas permeability is not predicted by Maxwell′s analysis.

A membrane for gas separation applications, which was prepared from poly(phenylene oxide) (PPO), showed higher CO_2 selectivity relative to other common gases [45]. In accordance to that, Hu, et al. [45] reported nanocomposite membranes prepared from brominated poly(phenylene oxide) (BPPO) and silica particles for CO_2 separations. The preparation of BPPO/silica nanocomposite membranes involved a physical blending of BPPO and an appropriate amount of silica. In this work, the membranes were prepared from three different sizes of silica (2, 10, and 30 nm) and different particles loadings. The membranes then were characterized in pure gas system to investigate their gas separation properties. In permeation study, the nanocomposites containing 0.3 wt% of 10 nm sized–silica showed the highest CO_2 permeability, that was by a factor of five relative to pure BPPO without a significant loss of CO_2 selectivity. The enhancement of CO_2 permeability was associated to the increase in free–volume of BPPO because the chain–packing was disrupted by the addition of the nanoparticles. It was expected qualitatively that the smaller–sized silica would have resulted in the highest permeability enhancement, because smaller silica particles have higher interfacial area than the larger one, so that increasing the polymer chain′s flexibility into a higher extent. However, this behavior was not observed, because the 2 nm–sized silica presumably had a different surface chemistry and a smaller surface area that might affect its performances relative to the other silica particles.

Poly(ether–*b*–amide) block copolymers, or well-known as Pebax®, have been con-

sidered potentially interesting for CO_2 removal applications [2, 20]. These copolymers exhibit a high CO_2selectivity over light gases and a high CO_2 permeability relative to other conventional rubbery or glassy polymers. This property is mainly the result of its high CO_2 solubility selectivity that is attributed to the strong affinity of the ether oxide linkages of the copolymers for CO_2. There are several attempts at developing nanocomposite membranes constituted from Pebax® as the polymer matrix.

Firstly, Zoppi, et al. [46] evaluated the effects of membrane morphology on gas separation performance of hybrid membranes prepared from Pebax® and inorganic fillers from silicon or titanium oxide. Hybrid films were prepared by sol–gel process that involves a polymerization of inorganic precursor in the solution where the polymer is priorly dissolved. Silicon oxide was prepared from tetraethoxysilane (TEOS), meanwhile titanium oxide was prepared from titanium tetraisopropoxide (TiOP). Based on the reaction condition used in this work, the obtained morphology in Pebax®/TEOS hybrid was different from Pebax ®/TiOP hybrid. As confirmed by field emission microscopy, TEOS fillers were finely distributed in Pebax® matrix. Depends upon the filler composition, the phase separation could be observed clearly in Pebax ®/TiOP hybrid. In accordance with the morphological differences, the gas transport behavior in each hybrid also occurred differently. Permeability of gases through a membrane is closely related to the compatibility and adhesion between the polymer and the filler particles. A good compatibility between polymer and fillers may result in decreased permeability, because the transport area reduces and the tortuous path for molecular transport increases. This case happened in Pebax®/TEOS hybrid where the polymer/filler phases were homogeneous. In Pebax®/TEOS hybrid, the gas permeability reduced as the increased filler content because the fillers contribute as barriers that reduces the gas transport. On the other hand, gas permeability in Pebax®/TiOP hybrid was less than the neat Pebax®. When the polymer

matrix was filled with 20–50 wt% TiOP particles, however, the gas permeabilities systematically increased. Pebax®/TiOP hybrid in which the phase–separation existed, the gas transport was favorably occurred in the phase separation–area and thus increasing the gas permeability. Despite of filler types, these hybrid films exhibited sufficiently high CO_2 permeabilities and selectivities depending on the polymer and filler compositions. For example, Pebax®/TEOS hybrid with 50 wt% filler content had CO_2/N_2 selectivity of 50 and CO_2 permeability of 20 Barrer.

Kim and Lee [47] also fabricated hybrid of Pebax® and silica by using sol–gel process. By polymerizing the TEOS in Pebax®, the transparent films were obtained as reported previously by Zoppi, et al. These hybrid membranes, however, showed different gas transport behavior. As the silica content increased, both CO_2 permeabilities and CO_2 selectivities over small permanent gases (i.e., He and N_2) also increased. For example, a hybrid containing 27 wt% of silica exhibited CO_2 permeability of 277 Barrer with $\alpha_{CO_2/He} = 8.6$ and $\alpha_{CO_2/N_2} = 79$ (comparing to a pure Pebax® film having CO_2 permeability of 122 Barrer with $\alpha_{CO_2/He} = 6.6$ and $\alpha_{CO_2/N_2} = 71$). The increase of permeability may be attributed to the increase of amorphous region that acts as the locus of the most gas transport in the membrane. The morphological changes at the interfaces of silica–PA block and silica–PE block gave rise to increased amorphous region in the membrane, as confirmed by X–ray diffraction and DSC analysis. Besides that, the interaction between the OH groups on the surface of silica phases with the polar CO_2 molecules, which observed from NMR and FT-IR analysis, might also contribute to the increased permeability. From gas permeation study, it was shown that α_{CO_2/N_2} and $\alpha_{CO_2/He}$ increased mainly due to the increased solubility selectivity.

Polyhedral oligomeric silsesquioxane (POSS) molecules have been investigated as candidate for dispersed phase in fabrication of nanocomposite membranes for gas separation applications. These molecules, with general structure of $(RSiO_{3/2})_8$ compounds, compose of cage-like structures with unreactive R groups that can be

functionalized in order to enhance their stability, compatibility, and solubility [48]. The R groups are various type organic groups, i.e., alkyl, olefin, alcohol, acid, amine, epoxy, and sulfonate. By appropriately matching these R groups with specific chemical moieties of the polymer chain, it is possible to obtain affinity between the polymer and the filler that leads to a nanocomposite membrane having finely dispersed filler.

Li and Chung [49] reported nanocomposite membranes prepared from Pebax® and POSS molecules. Hybrid films were prepared by solution blending method, and the homogeneous films were achieved by tuning the solvent evaporation rate. Two types of POSS molecules were used as filler particles, the octa(3–hydroxy–3–methylbutyldimethylsiloxane) POSS and the octa amid acid POSS, namely as POSS–OH and POSS–acid, respectively. It was shown that by incorporation of a small amount of POSS molecules, the CO_2 permeability and CO_2/H_2 selectivity were simultaneously increased. The enhancement of permeability arose from several factors. First, as confirmed by porosity analysis, the CO_2 molecules might pass through the large cavity of POSS molecules, which has lower resistance than the Pebax® matrix. Second, POSS particles presumably disrupted the chain packing of the Pebax® polymer, and in turn, increased the accessible free volume in polymer matrix. As shown by DSC graphs, T_g of hybrid films with low POSS content decreased relative to the pure Pebax®. This analysis confirmed that the polymer chain became more flexible, and the free volume enhanced as the polymer filled with POSS particles. When POSS loadings increased, however, the CO_2 permeability and CO_2/H_2 selectivity decreased. This phenomenon was attributed to the pore blockage and rigidification of the polymer chain. As POSS loadings were enhanced, a hydrogen bonding interaction between ether oxides (Pebax®) and hydroxy (POSS–OH) or carboxylic (POSS–acid) groups might hinder the mobility of the polymer chain and thus reducing the diffusion coefficients of the permeating gases.

From several nanocomposite membranes discussed above, it is clear that the

nanoparticle functionality also plays an important role in controlling the resultant gas transport properties of a nanocomposite membrane. Nanoparticles having specific chemical affinities with the penetrant gases could be introduced into a polymer matrix. In this way, it is expected that the chemical moieties would interact with the penetrant gas, so that facilitating the gas permeation through a membrane and enhancing the gas transport properties.

Regarding to this approach, Patel, et al. [40, 50] investigated the effect of nanoparticle functionality on gas transport properties of nanocomposites prepared from crosslinked–poly(ethyleneglycol). In this work, two types of fumed silica, fumed silica methacrylate–terminated and hydroxyl–terminated, namely FSma and FShy respectively, were introduced into poly(ethyleneglycol)diacrylate (PEGda) The addition of 10 wt% of fumed silica, either FSma or FShy particles, resulted in relatively small decreased CO_2 permeability. This behavior might be attributed to the more tortuous diffusion path passes by gas molecules in the presence of nonporous particle, finally reducing the CO_2 diffusivity. Nanocomposites containing FShy, however, showed more pronounced reduction on CO_2 permeability compared to that observed for FSma nanocomposites. Despite of decreased CO_2 diffusivity, this result could be expected if hydrogen bonding between hydroxyl groups at the surface of FShy and ether moieties of the PEGda chain were present in the nanocomposite that reduced the CO_2 solubility, and in turn, decreased the overall CO_2 permeability.

II.3 Composite Membranes for Gas Separation Applications

Dense polymeric membranes have taken much attention in commercial gas separation applications. The gas transport in dense membranes could be explained by the solution–diffusion mechanism. This intrinsic transport characteristic of a dense membrane controls the diffusivity and solubility of the permeating gases through the

membrane. In order to achieve a high productivity, that means a high permeability, the thickness of a dense gas separation membrane is often designed as low as possible. Nevertheless, this approach jeopardizes the mechanical strength of a dense membrane, especially when the membrane is used for high-pressure applications.

In order to eliminate this issue, anisotropic membranes have been developed. Anisotropic membranes, unlike dense membranes, consist of several layers each with different morphologies and gas transport properties. There are several types of anisotropic membranes such as phase separation membranes, interfacial polymerization membrane, and solution–coated composite membranes. A phase separation membrane, which firstly introduced by Loeb and Sourirajan [9], is one of the major breakthroughs in membane development. This membrane involves a single membrane material which has a pore density and size changing from layer to layers. Benefited from this morphology, the higher gas productivity could be achieved. Until now, this membrane has been widely used in reverse osmosis applications for water desalination. Following the success of Loeb–Sourirajan technique, asymmetric membranes for gas separation applications have been also investigated. It was found, however, most of the polymers for gas separation applications are difficult to be formed as asymmetric membranes.

This limitation encouraged the development of other anisotropic morphologies. A morphology found to be useful for gas separation applications is composite membranes prepared by solution–coating method. Typically, this membrane is prepared by coating one or more thin dense polymeric membranes on top of a microporous support (see figure II.3). The microporous support provides a mechanical integrity and a high permeability for gas transport, meanwhile the permselective mainly lies in the thin dense membranes. The formation and model used to describe the permeation properties in composite membranes will be briefly discussed in the remaining sections.

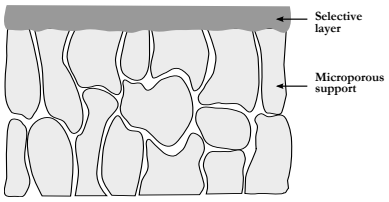


Figure II.3: Schematic of a composite membrane

II.3.1 Formation of composite membranes

The composite membranes are commonly prepared by applying a dilute polymer solution onto a microporous support. The processes of solution coating and production of porous support can be done separately. This process results in a composite membrane having one or more layers on top of a support. This method also provides means to achieve a composite membrane with each layers having its optimum performance. Although it seems like a simple method, there are several key issue that should be taken into considerations.

One of the most important factors is the state of the polymer when the solution is coated, whether it is glassy or rubbery [28]. A rubbery polymer is most commonly used to obtain a thin defect free membrane. Nevertheless, it is relatively difficult to prepare a defect free membrane by using a glassy polymer. This can be understood since the glass transition temperature is passed at a certain moment during the coating process. Furthermore, the large forces may be generated toward the solvent evaporation and consequently results in defects or leakages.

Another important feature is the number and the size of surface pores in the support. If the support has a high pore density, pore penetration will easily occur and thus add a significant resistance for gases permeation in this layer (the ideas about permeation resistance can be found in section II.3.2). As the result, the gas productivity and selectivity will decrease dramatically, even when the selective coating layer has no defects. Besides that, if the surface pores are too large, the incomplete coverage of the surface pores will cause defects after the evaporation reaches completion.

There are several useful attempts to prevent the incursion of a polymer solution into the support pores [51], i.e.,:

- For hollow fiber membranes, thermal annealing can be carried out before the coating of the selective layer. By applying the heat treatment, presumably, the surface and transition pores collapse, and thus reducing the pores size for the incursion paths of the selective polymer solution.

- Filling the pores with a mixture of non–solvent or other polymer before the coating layer is being applied. It was observed that this approach could even enhance the gas permeability without reduction on gas selectivity.

- Application of an intermediate layer or pre–coating layer form a high permeable polymer, a so–called gutter layer. Besides that, gutter layer also provides superficial pathways by which a penetrant easily pases toward the support.

- Application of a high concentration polymer solution or a higher molecular weight polymer to interlock the polymer coil on top of surface layer. However, this may result on reduction of the gas permeability, because the higher the concentration of polymer solution, the thicker the layer would be.

II.3.2 Resistance model of gas permeation

Henis and Tripodi [52] developed a model to predict the gas permeation properties in composite membranes, that was named as the resistance model. As the model's name implies, this model described the permeation in a membrane analogous to the flow of current in an electrical circuit. Each layer of composite membranes contributes to the total resistance to the gas permeation rate.

The permeation rate of a penetrant gas A through a polymeric membrane per

unit area per unit time is given by the following equation

$$Q_A = \Delta p_A \frac{P_A}{l} \tag{II.12}$$

where Q_A is the permeation rate of gas A, Δp_A is the pressure gradient of gas A across a membrane, P_A is the intrinsic permeability of a polymeric membrane to gas A, and l is the membrane thickness. The electrical current flowing through a resistor is described by Ohm′s Law, that is given by

$$I = \frac{E}{R} \tag{II.13}$$

Analogous to the Ohm′s Law above, the permeation rate of a penetrant, Q, is equivalent to the current, I, meanwhile the driving force for the current flow, E, is similar to the pressure gradient across a membrane, Δp. Thereby, the resistance to the permeate flow of gas A, R_A, can be equated with the electrical resistance, R, as follows

$$R_A = \frac{l}{P_A} \tag{II.14}$$

The equation II.14 above implies that the resistance is dependent upon several parameters such as the intrinsic properties of the polymer, the effective thickness (that correlates with the surface porosity of the support layer), the tortuosity of the pores in a polymer matrix, and the pressure of the permeate [52]. Nevertheless, by using this approach, the permeation properties of a composite membrane consisting of one or more thin dense layers could be modeled simply by adapting the construction and morphology this membrane to a series–parallel resistance model, as it will be shown in the following discussion.

First, we will consider a composite membrane consisting of a thin defect–free selective layer backed by a highly–microporous support. Surface porosity, which is

equal to the ratio of the total pores area to the membrane area, is one of the critical factors in controlling the permeation process, whether it will take place mainly in the coating/selective layer or in the support layer of a composite membrane. In the present system, the selective layer will determine the total resistance of the gas permeation, and thus the gas transport properties. An illustration of the composite membrane discussed here is shown in figure II.4.

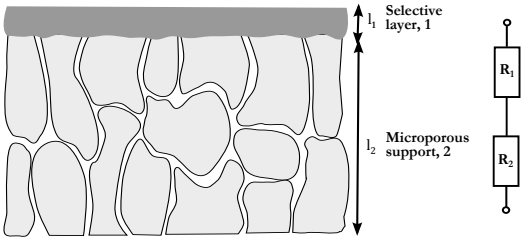


Figure II.4: Illustration of cross–sectional morphology of the composite membrane having a defect-free layer on top of a highly–microporous layer and its corresponding electrical circuit analogue

Based on this system, resistances in series can be used to predict the permeation of gas A through the membrane

$$R_{t,A} = R_{1,A} + R_{2,A} \tag{II.15}$$

where R_t is the total resistance for gas A, equation II.12 then can be expressed as follows

$$Q_A = \Delta p \left(\frac{l_1}{P_{1,A}} + \frac{l_2}{P_{2,A}} \right)^{-1} \tag{II.16}$$

so that the separation factor of gas A relative to gas B then can be written as follows

$$\alpha_{A/B} = \frac{Q_A}{Q_B} \tag{II.17}$$

$$\alpha_{A/B} = \frac{l_1/P_{1,B} + l_2/P_{2,B}}{l_1/P_{1,A} + l_2/P_{2,A}} \tag{II.18}$$

If the support layer has a high surface porosity, it can be assumed that the gas trans-

port in this layer occurred by Knudsen diffusion and/or convective flow. In this regard, the resistance to the permeation rate will arise mainly from the selective layer, given that $l_1/P_{1,A} \gg l_2/P_{2,A}$ and $l_1/P_{1,B} \gg l_2/P_{2,B}$. The equation II.18 now can be written as follows

$$\alpha_{A/B} = \frac{l_1/P_{1,B}}{l_1/P_{1,A}} = \frac{P_{1,B}}{P_1, A} \tag{II.19}$$

It should be kept in mind that this assumption might not be applicable in actual applications. By using equation II.17 detailed above, however, Pinnau, et al. [53] showed that the theoretical CO_2/N_2 and O_2/N_2 selectivity of a polysulfone–silicone rubber composite membrane was in good agreement with the experimental data.

In another case, the composite membrane could also be constructed from a asymmetric membrane having a low surface porosity, i.e., $< 10^{-4}$, topped by a highly permeable sealing layer. Before the pores or defects in the surface are plugged by sealing polymer, the gas permeation of the asymmetric membrane will occur by convective flow or Knudsen diffusion through the pores.

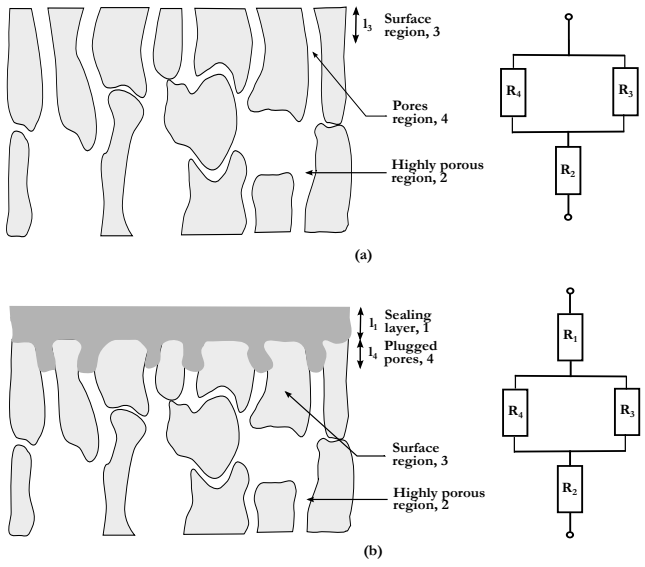


Figure II.5: Illustration of cross–sectional morphology of membranes with their corresponding electrical circuit analogue (a) an uncoated membrane (b) a coated membrane

As shown in figure II.5, the resistance model for gas A in the uncoated membrane

is given by

$$R_{t,A} = \frac{R_{3,A}R_{4,A}}{R_{3,A} + R_{4,A}} + R_{2,A} \tag{II.20}$$

If it is assumed that the resistance in the high porous region, R_2, can be neglected, the equation II.20 reduces to

$$R_{t,A} = \frac{R_{3,A}R_{4,A}}{R_{3,A} + R_{4,A}} \tag{II.21}$$

so that, the permeation rate can be expressed as

$$Q_A = \Delta p \left(\frac{l_3}{P_{4,A}(\varepsilon)} + \frac{l_3}{P_{3,A}(1-\varepsilon)} \right)^{-1} \tag{II.22}$$

where ε is the surface porosity. By taking the same assumption, the permeation rate in a coated membrane can be expressed as

$$Q_A = \Delta p \left(\left(\frac{l_3}{P_{3,A}(\varepsilon)} + \frac{l_4}{P_{1,A}(1-\varepsilon)} \right) + \frac{l_1}{P_1} \right)^{-1} \tag{II.23}$$

By coating a thin of a highly–permeable silicon rubber layer on top of a polysulfone assymetric membrane, Henis and Tripodi [52] showed that this approach could increase the selectivity of the polysulfone membrane while keeping the gas permeability almost intact. In uncoated membrane, most of the gas will pass through the pores by Knudsen diffusion mechanism that is characterized with a low separation performance. It can be understood because the open pores have a much higher permeability than the polymer matrix. After the coating, the resistance of the pores increases by many orders of magnitude leading to the increase of separation performance.

Lundy and Cabasso [54] developed a multilayer composite membrane having different construction from other composite membranes discussed above. This composite membrane involves a microporous support layer, an intermediate layer, and a

thin dense selective layer. The intermediate layer functions as extra channel for gases to permeate toward the surface of a support layer. The schematic morphology of this membrane is depicted in figure II.6.

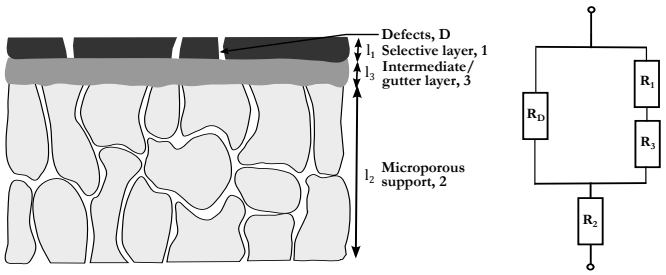


Figure II.6: Illustration of cross–sectional morphology of the multilayer composite membrane with its corresponding electrical circuit analogue

In preparation of a thin dense selective layer, defects such as pinholes are hardly to avoid, especially when the membrane is prepared from a glassy polymer. If defects are present, most of gas will permeate with lower resistances through the defects, and thus it reduces the gas separation performance. In this work, they showed that this phenomenon could be prevented by the use of an intermediate layer. An intermediate layer could plug the viscous flow from the selective layer and could retain the gas selectivity into some extent.

Based on work of Lundy and Cabasso, the resistance model in which the contribution of defects in the surface of the selective layer will be given here. If it is assumed that the resistance in a support layer is negligible, and the total resistances from a selective layer and an intermediate layer can be indicated as R_C, where $R_C = R_1 + R_3$, the total resistance to the permeation of gas A per unit area then can be derived as follows

$$R_{t,A} = R_{C,A} + R_{D,A} \tag{II.24}$$

$$R_{C,A} = R_{1,A} + R_{3,A} = \frac{l_1}{P_{1,A}A_1} + \frac{l_3}{P_{3,A}A_1} \tag{II.25}$$

where A_1 is the surface area of the selective layer excluding the defects. Meanwhile

the resistance of the intermediate layer which is exposed by defects is

$$R_{D,A} = \frac{l_3}{P_{3,A} A_D} \tag{II.26}$$

where A_D is the area exposed by defects.

Thereby, combining equation II.25 and equation II.26, the total resistance is then written by

$$R_{t,A} = \frac{\left(\frac{l_1}{P_{1,A} A_1} + \frac{l_3}{P_{3,A} A_1}\right)\left(\frac{l_3}{P_{3,A} A_D}\right)}{\frac{l_1}{P_{1,A} A_1} + \frac{l_3}{P_{3,A} A_1} + \frac{l_3}{P_{3,A} A_D}} \tag{II.27}$$

In order to simplify the equation above, A_D/A_T is defined with the term f, the defect ratio of the membrane, so that equation II.27 becomes

$$R_{t,A} = \frac{\left(\frac{l_1}{P_{1,A}(1-f)} + \frac{l_3}{P_{3,A}(1-f)}\right)\left(\frac{l_3}{P_{3,A} f}\right)}{\frac{1}{1-f}\left(\frac{l_1}{P_1} + \frac{l_3}{P_3}\right) + \frac{l_3}{P_3 f}} \tag{II.28}$$

Clearly, the surface properties or defects could reduce the effectiveness of composite membrane. In order to make the use of the selective layer, for a rule of thumb, more than 90% of the resistances should lie in the selective layer [51].

Chapter III

Experiment

III.1 Dense Mixed Matrix Membranes

III.1.1 Preparation of Dense Mixed Matrix Membranes

Materials

Pebax® MH 1657 block copolymer containing 60 wt% polyethylene oxide (PEO) and 40 wt% polyamide–6 (PA–6) was purchased from Arkema. PEG POSS® Cage Mixture with a product number of PG–1190 was purchased from Hybrid Plastics, Inc. The chemical structures of Pebax® block copolymer and PEG POSS® molecule are depicted in figure III.1 and figure III.2, respectively. Ethanol absolute (99%) was purchased from Analar Normapur and Acros Organics. 1,4–Dioxane anhydrous (95%) was purchased from Sigma–Aldrich. All these chemicals were used without further purification.

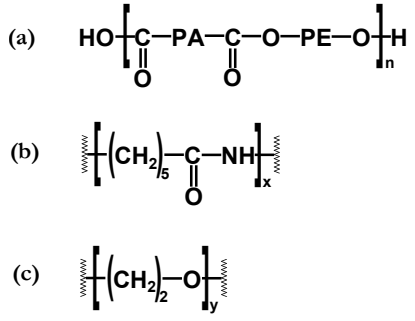
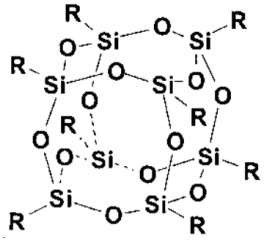


Figure III.1: Chemical structures of (a)Pebax®, where (b) PA is polyamide and (c) PE is polyethylene oxide ([2])



R = -$CH_2CH_2(OCH_2CH_2)_mOCH_3$

$(C_{2m+3}H_{4m+7}O_{m+1})_n(SiO_{1.5})_n$
n = 8, 10, 12 (n = 8 is shown here)
m = ~13.3

Figure III.2: Chemical structure of PEG POSS® cage mixture ([3])

Film preparation

Dense neat Pebax® membranes (as control samples) and dense Pebax®/PEG POSS® mixed matrix membranes containing different PEG POSS® concentrations were fabricated by a solution–casting method. The polymer solution was prepared using two types of solvent mixtures; first, a mixture of ethanol/water of 70/30 wt% and ethanol/water/1,4–dioxane of 65/30/5 wt%. Pebax® with concentration of 2 wt% then was dissolved by heating at temperature range of 50–60 °C and stirring for 3 hours. The obtained polymer solution was filtered through a steel filter with pore size 32 μm to remove impurities. Subsequently, the stipulated amounts of PEG POSS® molecules were added into the solution and stirred for 1 hour. The homogeneous solution was then poured into a teflon ring mold. To facilitate the solvent evaporation, the solution was dried in an oven at 40 °C by partly covering it with a glass dish for 4 days. After the slow evaporation of the solvent, the membranes were formed. To remove the residual solvents, the membranes were dried in a vacuum oven at 80 °C for 3 days. Finally, the thickness of dense membranes was measured by a digital caliper (Fowler ProMax Caliper), and they varied from 60 to 100 μm.

III.1.2 Characterization of Dense Mixed Matrix Membranes

Differential scanning calorimetry (DSC)

The thermal properties (glass transition temperatures, T_g) of dense membranes were analyzed using a DSC (Differential Scanning Calorimetry) method on DSC Q2000 TA Instruments. Firstly, the dense membranes were stored under vacuum at 80 °C for 1 day to remove the moistures. Small pieces of a testing membrane then placed into an aluminum DSC pan. After the sample preparation, the T_g measurement was done by running two DSC cycles in temperature range of –80 °C to 50 °C at a scan rate of 10 °C/min under a nitrogen purge gas stream. In the first DSC cycle, the sample was heated from –80 °C to 50 °C to obtain the first thermogram, and then the cycle was completed by cooling down from 50 °C to –80 °C. Finally, the second DSC cycle was carried out by repeating the same procedure as in the first cycle.

The DSC output plots the enthalpic changes and peaks relating to endothermic and exothermic transitions. T_g can be determined at the point where the heat capacity, ΔC_p, is increased by one–half [55]. In this experiment, T_g was estimated as the midpoint temperature in the transition region owing to the increase of heat capacity in the first scan thermogram. The increase in ΔC_p is associated with the increase of polymer's molecular motion [55]. Thereby, DSC offers qualitative approach to investigate the effect of nanoparticles addition on the polymer flexibility that is associated with the free volume exists in the polymer matrix.

III.2 Mixed Matrix Composite Membranes

III.2.1 Preparation of Mixed Matrix Composite Membranes

Materials

A polyacrylonitrile (PAN) asymmetric porous support was supplied from GMT Membrantechnik GmbH, Rheinfelden, Germany. Poly(trimethylsilyl)propyne (PTMSP)

was purchased from Gelest, Inc. The chemical structure of PTMSP is given in figure III.3. Hexane anhydrous (95%) was purchased from Sigma–Aldrich. Both chemicals were used as received. Other chemicals used for preparation of mixed matrix composite membranes, including, Pebax®, PEG POSS®, ethanol absolute, and 1,4–dioxane, were detailed in section III.1.1.

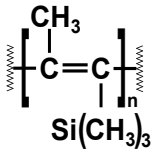


Figure III.3: Chemical structure of poly(trimethylsilyl)propyne ([4])

Composite Preparation

A single–layer and multilayer composite membranes were fabricated using a solution–coating method in which one or more thin–dense polymeric layers were cast onto a support.

Single-layer composite membranes

A single–layer composite membrane involves a selective layer coated on a PAN porous support. The selective layer was prepared from neat Pebax®. The preparation of Pebax® or Pebax/PEG POSS® homogeneous solution was detailed on section III.1.1. After preparing the polymer solution, the solution could be readily cast onto the surface of a PAN support by stroking a sponge–brush (Poly-brush® from Jen Manufacturing, Inc.), which was previously dipped into the solution, over the support′s surface. The composite membranes then were dried at atmospheric condition for an overnight.

To prevent the intrusion of selective polymer into the pores of a support layer, the pre–coating of ethanol/water mixtures before the coating of a selective layer was investigated. The ethanol/water mixtures of 70/30 wt% was applied onto a support using the same method as mentioned previously. After the pre-coating layer

became slightly dry, the polymer solution was directly coated over the pre–coating layer forming a composite membrane. Finally, the obtained composite membranes were mold and cut into circles having radius of 2 cm for gas flux measurements.

Multilayer composite membranes

Unlike a single–layer composite membrane construction, a multilayer composite membrane was constructed from a PAN support layer, a gutter layer, and a selective layer. Here, the gutter layer was prepared from solution of PTMSP (1 wt% in hexane). The solution was prepared by heating at the temperature range of 45–55 °C and stirring for 2 hours. After cooling down the solution, it was then filtered through a steel filter (the pore size 32 μm). Subsequently, the PTMSP solution could be readily coated onto the surface of a PAN support using a sponge–brush that was previously dipped into the solution. The gutter layer then was dried at atmospheric condition for 5–6 hours before the coating of a selective layer. The selective layer was prepared either from pure Pebax® or Pebax/PEG POSS® with different POSS concentrations. The selective layer then was applied on top of the gutter layer by using the same way as described in previous section.

III.2.2 Characterization of Mixed Matrix Composite Membranes

Scanning Electron Microscopy (SEM)

The morphologies of the composites were observed by using scanning electron microscopy (SEM). First, the samples were fractured in liquid nitrogen and were coated with gold by sputtering (the coating layer was ± 2 micron). The cross-sectional analyses then were done with Magellan™SEM instrument, and the membrane thickness was measured using the digital image analysis.

Gas flux measurement

The gas transport property of composite membranes was investigated using a constant–pressure variable–volume (or continuous flow) method [56]. This method is

commonly carried out to study higly–flux membranes such as thin dense polymeric membranes and composite membranes [56], as investigated in this work. The apparatus for this method is illustrated in figure III.4

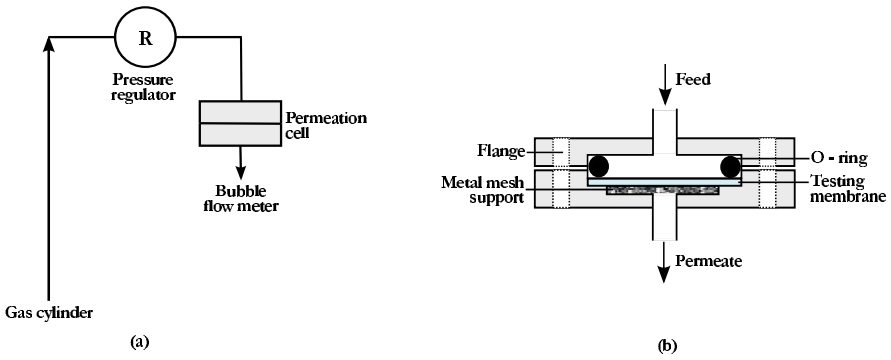


Figure III.4: Illustration of (a) a constant–pressure variable–volume apparatus for gas flux measurement and (b) a gas permeation cell

In this work, the membranes were tested in the pure gas system using the sequence of N_2 and CO_2. The gas flux of N_2 was measured at pressures range of 100–500 kPa and room temperature, meanwhile the gas flux measurement for CO_2 was performed at pressures ranging 100–300 kPa and room temperature. The gas flux measurements were replicated two or three times with the difference for each membrane was $\pm$ 1%.

Subsequently, the permeation rate for gas A is defined as follows

$$Q_A = \frac{V}{A.t.\Delta p} \tag{III.1}$$

where V is the displaced volume of a soap film in the bubble flow meter for a particular time (in m^3), A is the surface area of a testing membrane (in m^2), t is the time required for displacement of a soap film (in *second*), and Δp is the pressure difference between the working gauge pressure (in pressure regulator) and the atmospheric pressure (in kPa).

For the measurement of the gas permeation rate above, the true value was estimated within the interval $Q \pm 5\%$.

Finally, the gas selectivity can be determined as follows

$$\alpha_{A/B} = \frac{Q_A}{Q_B} \tag{III.2}$$

where Q_A and Q_B refer to the permeation rate of gases A and B.

Chapter IV

Result and Discussion

IV.1 Dense Mixed Matrix Membranes

IV.1.1 Preparation and Characterization of Dense Mixed Matrix Membranes

The dense membranes were prepared using two types of solvent mixtures, ethanol/-water of 70/30 wt% and ethanol/water/1,4–dioxane of 65/30/5 wt%, with the compositions detailed in table IV.1. All these dense membranes were transparent. The optical transparency could be a good indicator for the homogeneity between the polymer and the filler particles [47], in this case, this might be due to the presence of hydrogen bonding interaction between ether oxide linkages of Pebax® copolymer and ether oxygen atoms in PEG groups of POSS particles [57]. Nevertheless, upon the polymer/filler composition was 50/50, the surface of dense membranes were rather sticky. From independent studies, it was shown that POSS networks could have a low surface energy, and when POSS particles were introduced into a hybrid system, they lowered the surface energy of the system [57, 58]. Changes on the surface energy might be followed by the redistribution of the polar groups in the surface. The polar PEG groups of POSS particles presumably dominated the surface of Pebax® chains and caused the redistribution of polymer chains in the membrane interface. As the result, the distribution of POSS particles in the interface increased and caused the surface sticky. However, another analysis, i.e., surface contact angle measurement, should be provided to support this phenomenon.

Table IV.1: Compositions for preparation of dense membranes

Samples	Pebax® /PEG POSS® composition	Observation 1[a]	Observation 2[b]
Pebax®	100/0	Transparent	Transparent
PPOSS1	91/9	Transparent	Transparent
PPOSS2	83/17	Transparent	Transparent
PPOSS3	50/50	Transparent, sticky small agglomeration	Transparent, sticky
PPOSS4	40/60	Transparent, sticky small agglomeration	Transparent, sticky

[a]Prepared by ethanol/water of 70/30 wt%
[b]Prepared by ethanol/water/1,4–dioxane of 65/30/5 wt%

Dense membranes prepared by solvent mixture of ethanol/water/1,4–dioxane do not show any particles agglomeration. Thereby, it is of interest to study the effect of this solvent mixture on particle dispersion. Theoretically, a specific solvent behavior toward molecules, i.e., polymer, can be explained in terms of solubility parameter. As a rule of thumb, if the solubility parameter of a given solvent is equal to the solubility parameter of a given molecule, the dissolution of a molecule will be favored. To analyze the contribution of solvent mixtures to the POSS particle dispersion, firstly, the calculation for each solubility parameter of POSS particle and solvent mixtures will be carried out. In this study, the solubility parameter of PEG POSS® will be calculated on the basis of Maxwell relationship (equation IV.1) and a correlation between the dielectric constant and solubility parameter developed by Darby (equation IV.2) [59], because the corresponding data were provided by the manufacturer [60].

$$\varepsilon = n^2 \tag{IV.1}$$

$$\delta = 7.0\varepsilon \tag{IV.2}$$

where n is the refractive index of a given material, ε is the dielectric constant, and δ is the solubility parameter. Based on these equations, the solubility parameter of PEG POSS® is 14.72 $MPa^{1/2}$.

The solubility parameter of the solvent mixtures can be calculated by using the Hoftyzer and Van Krevelen method [59] in which the contribution of dispersion, polar, and hydrogen bonding solubility parameters are taking into account in the total solubility parameter, that is

$$(\delta_t)^2 = (\delta_d)^2 + (\delta_p)^2 + (\delta_h)^2 \tag{IV.3}$$

Table IV.2: Thermodynamic solubility parameters of ethanol, water, and 1,4–dioxane

Solvent	δ_d	δ_p	δ_h	δ_t
	$(MPa^{1/2}) \pm 5\%$			
Ethanol	15.8	8.8	19.5	26.6
Water	12.3	31.3	34.2	48
1,4–dioxane	19.1	1.8	7.4	20.6

Based on the solubility parameters given above, the solubility parameter of ethanol-/water (70/30 wt%) mixture is 33 $MPa^{1/2}$, meanwhile the solvent mixture of ethanol-/water/1,4–dioxane (65/30/5 wt%) has solubility parameter of 32.7 $MPa^{1/2}$ that is quite similar with the previous one. In terms of solubility parameter, it may imply that the addition of 1,4–dioxane into the ethanol/water mixture does not significantly affect the filler dispersion. Nevertheless, the correlation between solvent and fillers (i.e., solid particles) dispersion in hybrid system can be explained by using the liquid–solid interaction strength parameter, ε^o [61]. The solvent strength, which is quantified by the solubility parameter, is less dependent upon the type of filler particles, but the ε^o could vary dependent upon the filler phase [62]. Unlike the solubility parameter, the ε^o for solvent mixtures also does not vary linearly with the solvent composition [62]. The interaction between a given solvent and filler particles increases with the increased ε^o. Probably, this is the case when a small amount of 1,4–dioxane was added into the solvent mixtures of ethanol/water. The 1,4–dioxane presumably increased the ε^o and enhanced the solvent interaction with the siloxane cage and thus leading to the more dispersed filler phase. Thereby, the particle ag-

glomeration was not observed in dense membranes prepared from solvent mixture of ethanol/water/1,4–dioxane, even when polymer and filler compositions were 50/50 or more.

In the next experimental study, the hybrid system discussed here would be cast in a support layer to form a composite membrane construction. Thereby, it is important that the solvent of casting solution would not destroy the polymer support. In this case, 1,4–dioxane is a good choice since this solvent does not dissolve polyacrylonitrile (PAN) support [23].

The thermal properties of dense membranes were characterized using DSC analysis. The DSC measurement in this study is shown in table IV.3.

Table IV.3: Thermal properties of Pebax® and Pebax®/ PEG POSS® membranes

Samples	Pebax®/ PEG POSS® composition	T_g (^oC)	T_m of PEO (^oC)
Pebax®	100/0	–63.73	5
PPOSS1	91/9	–60.96	9
PPOSS2	83/17	–57.23	9
PPOSS3	50/50	not detected	9
PPOSS4	40/60	not detected	9

During the DSC measurement, the T_g and T_m of PEO segments were observed. The T_m as well as T_g of PA blocks, however, were out of the temperature range observation. Here, the T_g and T_m of PEO blocks closely fit with the reported data from other independent studies. As commonly reported, the variation of T_g can be attributed to the change of the excess free volume available in a polymer, which resulted from changes of polymer chain packing or chain flexibility. The higher the polymer chain mobility, the higher the free volume exists in a polymer that is commonly indicated by reduction of T_g. In this study, the addition of PEG POSS® resulted in higher T_g value. This might imply that the existing free volume in Pebax® reduced by the addition of PEG POSS® particles.

Car, et al. [63] studied a hybrid of Pebax®/PEG that is quite comparable to the

hybrid system studied here. It was reported that the incorporation of low molecular weight PEG molecules into Pebax® matrix resulted in decreased T_g. In the opposite, the incorporation of PEG POSS® in the present study resulted on higher T_g relative to the pure Pebax®. It can be understood since in Pebax®/PEG POSS® system here, the siloxane cage structure were present and thus retarding the molecular motion of the polymer chains and hinder the polymer mobility [64]. As the result, the excess free volume was decreased, and T_g increased. The change of excess free volume commonly follows by the alteration of gas transport properties of a membrane, as it will be discussed on the following section.

IV.1.2 Model for Gas Permeation in Dense Mixed Matrix Membranes

The gases permeation of dense mixed matrix membranes was modeled using the Maxwell's analysis given in section II.1.2. Based on this model, the CO_2 and N_2 permeabilities in hybrid Pebax®/PEG POSS® are depicted in figure IV.1.

Maxwell model predicts that the addition of impermeable fillers in a polymer matrix will reduce the gas transport properties of a membrane. The reduced permeability may be attributed to the loss of excess volume available for penetrant transport and the increased tortuousity of the diffusion pathways passed by the penetrant molecules [1]. In this study, the gas transport properties (i.e., the gas permeability) of the dense mixed matrix membranes were not investigated. Since the experimental data was not available, the permeation model was developed by using data from another independent study. As it is shown, the gas permeability decreases as the filler concentration increases. The same trend was observed for the gas permeation rate in the hybrid multilayer composite membranes (as it will be discussed in the following section). Thus, it implies that the Maxwell model could also be useful to explain the gas permeation behavior in composite membranes.

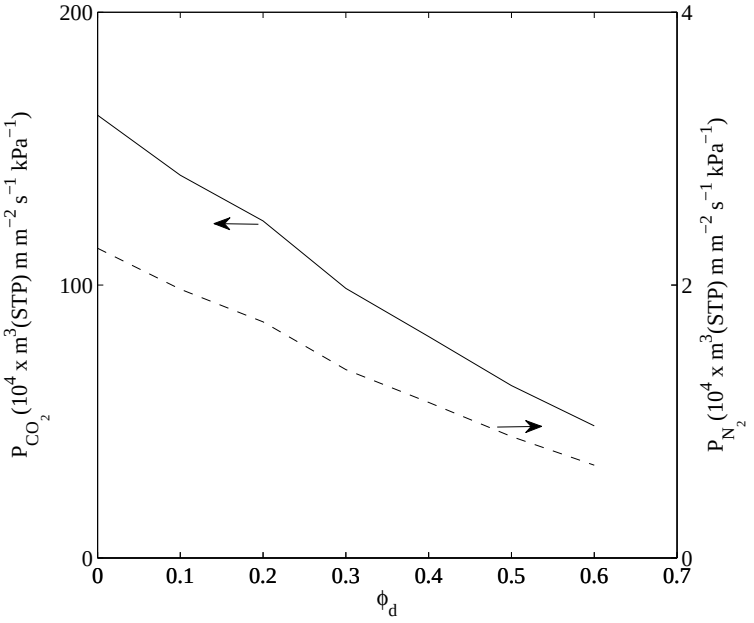


Figure IV.1: Theoretical model for Pebax®/PEG POSS® hybrid. The permeability data for pure Pebax® was taken from Kim, et al. ([5])

IV.2 Composite Membranes

IV.2.1 Single–layer Composite Membranes

Here, a single layer composite membrane was prepared by casting the Pebax® solution on the surface of a PAN porous layer by hand. Concentration of the solution was varied in the range of 0.5 wt% to 2 wt% in order to find the optimum concentration that will be used for preparation other membranes. The obtained composite membranes then were characterized using the gas flux measurement to study their gas transport properties. The gas flux measurement was carried out in a pure gas system using N_2 and CO_2 gases in sequence. The results are shown in the table IV.4.

In this study, the CO_2 permeation rate decreased with increased Pebax® concentration, whereas the membrane selectivity toward CO_2 gas increased with polymer concentration. In the case where the resistance of the support layer can be neglected, the permeation properties in a single layer composite membrane will be mainly con-

Table IV.4: Permeation properties of PAN–Pebax® composite membranes

Pebax® concentration (wt%)	Q_{CO_2} $(10^{-6} \cdot m^3 m^{-2} s^{-1} kPa^{-1})^a$	α_{CO_2/N_2}
0.5	144.7	1
1	14.2	1
1.5	0.5	21
2	0.7	37

$^a cm^3 cm^{-2} s^{-1} cmHg^{-1} = (1.33 \cdot 10^2) m^3 m^{-2} s^{-1} kPa^{-1}$

trolled by the properties of the coating layer. Thereby, the permeation properties of the composite membrane studied here will be discussed in terms of the permeation of the Pebax® coating layer.

Permeation rate is the inverse function of membrane thickness, thereby permeation rate decreases when the layer thickness increases. Here, when the concentration was increased, it appeared that the layer thickness also increased, and thus resulting on decreased permeation rate. As confirmed by SEM, the cross–sectional morphologies analyses showed that the composite membranes in the order of thickness, from the less to the most, are: Pebax with concentration ® of 0.5 wt% (thickness <0.1 μm), 1 wt% (thickness of 0.1–0.2 μm), 1.5 wt% (thickness of 0.2–0.3 μm), and 2 wt% (thickness of 0.3–0.4 μm). The SEM images of these composite membranes are shown in figure IV.2.

The α_{CO_2/N_2} in low–concentration membranes was very low. It may be understood since in dilute–concentration solutions, the polymer coils could easily penetrate into the pores of the support layer. Subsequently, the pores will be blocked, so that leading to a significant loss of membrane selectivity even when the polymer intrusion only a few micron depth [51]. The decreased membrane selectivity may be attributed to the increase of the resistance in the support layer, so that the support layer resistance can not be longer neglected. On the other hand, in high–concentration membranes, the selectivity can be retained. Probably, the more concentrated solu-

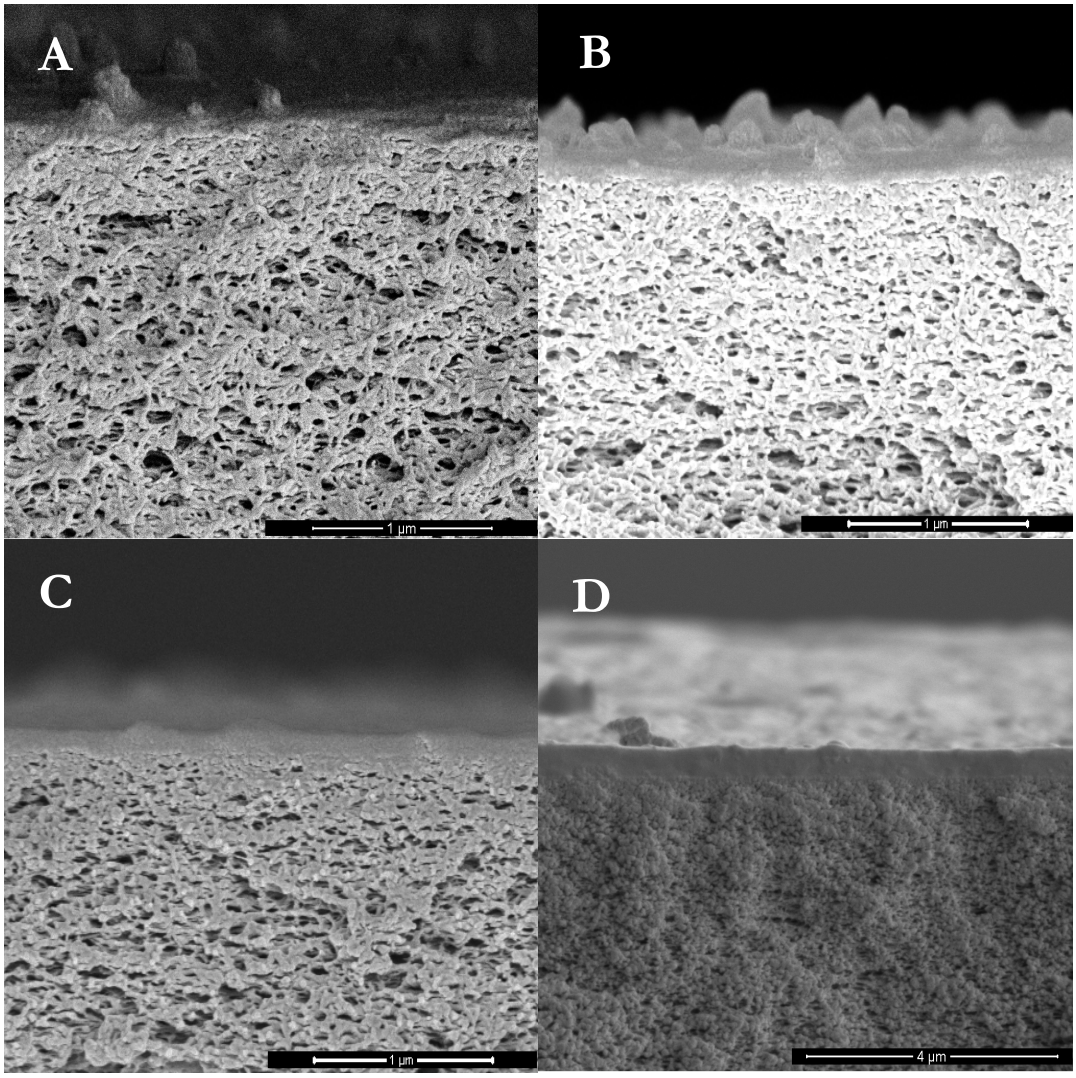


Figure IV.2: Cross–sectional morphologies of PAN–Pebax® composite membranes with Pebax® concentrations of (a)0.5 wt% (b)1 wt% (c)1.5 wt% and (d)2 wt%

tions could interlock the polymer chains, so that polymer could not easily penetrate into the support pores [51]. Nevertheless, it appeared that the membrane from solution of 2 wt% had permeation rate lower than that of other data reported in open literature (i.e., a study by Blume et al. [65]). We can assume that the defects were not present in the coating surface. If the surface has defects, the permeation rate should be higher because the permeation process will take place by Knudsen flow or convective flow. The pore blockage by intrusion of polymer coils presumably was also responsible in decreased permeation rate observed here.

Due to the pore blockage, some strategies were further investigated to prevent the intrusion of polymer into the support pores. First, it can be done by filling the support pores with the non–solvent mixture before the casting of the selective layer. Here, the non–solvent mixture was prepared from ethanol/water of 70/30 wt%, because this mixture is compatible with the coating solution and does not destroy the PAN support layer [23]. To prepare the composite membrane, the ethanol/water mixture was firstly applied to the surface of PAN layer. After the solvent became slightly dry, the Pebax® solution with different concentrations was coated over the pre–coating of non–solvent mixture. The gas permeation properties of these membranes were then measured using the gas flux measurement. The results are presented in table IV.5.

Table IV.5: Permeation properties of PAN–Pebax® composite membranes (effect of the pores support filling by a non–solvent mixture)

Pebax® concentration (wt%)	Q_{CO_2} $(10^{-6} \cdot m^3 m^{-2} s^{-1} kPa^{-1})^a$	α_{CO_2/N_2}
0.5	60.3	1
1	36.2	1
1.5	1.2	20
2	0.9	31

$^a cm^3 cm^{-2} s^{-1} cmHg^{-1} = (1.33 \cdot 10^2) m^3 m^{-2} s^{-1} kPa^{-1}$

As can been seen in the table IV.5, the gas transport properties of composite membranes prepared by pre–coating of non–solvent mixtures are almost similar with the composite membrane prepared without the same treatment (detailed in table IV.4). Likewise, the permeation rate decreased as the increased solution concentration. Nevertheless, membranes prepared from solution with concentration of 1, 1.5, and 2 wt% showed higher permeation properties than the ones prepared without applying the non–solvent mixture. By this approach, the permeation rate increased by a factor of two.

In the situation where the non–solvent is incorporated into the support layer, it is assumed that the selective layer will be partially dried due to the presence of deposited solution below it [66]. The partial drying process will produce a selective layer having an asymmetric morphology in which the pore density changes over the layer [66]. Thereby, the said selective layer will have a porous region adjacent to the porous support, a less porous region, and a dense skin in the outer layer. As the asymmetric membrane nature, the porous region will readily pass more penetrants and thus enhancing the permeation rate, as it is observed here. However, the increased permeation rate is coupled with decrease in gas separation properties. Presumably, the selective region in such an asymmetric selective layer is thinner and could not accommodate high separation loading as well as a dense selective layer having the same thickness.

IV.2.2 Multilayer Composite Membranes

Besides the application of non–solvent mixture, a gutter layer can also be introduced between the selective layer and the support to prevent the polymer intrusion into the support pores. A gutter layer is often prepared from a highly–permeable polymer. Because its high permeability characteristic, a gutter layer will readily transport the penetrants toward the support layer so that the permeation rate will be kept almost intact. The gutter layer was prepared from 1 wt% poly(trimethylsilyl)propyne (PTMSP)

in hexane. The PTMSP was directly cast on the surface of the PAN support. The Pebax® selective layer was then applied after the gutter layer dried. The obtained composite membrane would be constructed from PAN support layer, PTMSP gutter layer, and Pebax® layer on top of the membrane. The gas permeation properties of multilayer composite membranes are given in the table IV.6.

Table IV.6: Permeation properties of Pebax® multilayer composite membranes (effect of the PTMSP gutter layer)

Pebax® concentration (wt%)	Q_{CO_2} $(10^{-6} \cdot m^3 m^{-2} s^{-1} kPa^{-1})^a$	α_{CO_2/N_2}
0 (control)	20.9	3
0.5	3.3	41
2	0.7	61

$^a cm^3 cm^{-2} s^{-1} cmHg^{-1} = (1.33 \cdot 10^2) m^3 m^{-2} s^{-1} kPa^{-1}$

The CO_2 and N_2 (not shown here) permeation rates of the control sample were in good agreement with the reported data in open literature [67]. However, it should be noted that the permeation rate of those gases might be varied from one literature to another, because the gas transport properties in PTMSP polymer are dependent upon the properties of the casting solvent [68]. It was suggested that the PTMSP polymer had a microporous nature [69] and showed very high gases permeability. Due to these characteristics, it is of interest to study the gas transport properties of a composite membrane when PTMSP used as the gutter material.

As it can be seen in table IV.6, the multilayer composite membranes exhibited higher gas transport performances relative to the PAN–Pebax® composite membranes. Interestingly, the multilayer composite membrane prepared from 2 wt% polymer solution showed CO_2 permeation rate as similar with the PAN–Pebax® composite membrane having the same concentration, that was $0.7 \cdot 10^{-6} m^3 m^{-2} s^{-1} kPa^{-1}$. In this multilayer composite membrane, the α_{CO_2/N_2} even enhanced two times higher compared to the previous one. This case provides evidence that the gutter layer might

be effective to prevent the polymer incursion into the pores support, as well as to facilitate the transport of penetrants across the membrane [54, 70, 67]. In the same time, the gutter layer also provides smooth surface for depositing the selective layer, so that a selective layer with uniform thickness can be achieved [70]. As the results, the gas separation performance of the selective layer enhanced.

IV.2.3 Mixed Matrix Composite Membranes

A mixed matrix composite (MMC) membrane refers to a multilayer composite membrane in which the hybrid Pebax®-PEG POSS® was used as the top selective layer material. MMCs were comprised of PAN support layer, PTMSP gutter layer, and Pebax®/PEG POSS® selective layer. The hybrid selective layers were prepared with different concentrations of Pebax® and PEG POSS ® loadings. The compositions used to prepare MMCs and their corresponding gas permeation properties are shown in table IV.7.

Table IV.7: Permeation properties of mixed matrix composite membranes

Pebax® concentration (wt%)	PEG POSS® content (wt%)	Q_{CO_2} $(10^{-6} \cdot m^3 m^{-2} s^{-1} kPa^{-1})^a$	α_{CO_2/N_2}
0.5	0 (control)	3.3	41
	0.01	2.7	33
	0.1	1.6	35
	0.5	1.3	43
2	0 (control)	0.7	61
	0.2	0.7	71
	0.4	0.4	66
	2	0.4	58

$^a cm^3 cm^{-2} s^{-1} cmHg^{-1} = (1.33 \cdot 10^2) m^3 m^{-2} s^{-1} kPa^{-1}$

From table IV.7, it was found that the incorporation of PEG POSS® into the Pebax® matrix resulted on the slight increase of the gas separation properties, particularly, in the MMCs membrane prepared from 2 wt% of Pebax® and POSS content of

0.2 wt%. The increased selectivity toward CO_2 probably due to the increased affinity for CO_2 as ether oxide moities were enhanced by the addition of PEG POSS® into the polymer matrix.

For membranes with 2 wt% of Pebax®, however, as the filler content was enhanced, the gas permeation rate and the CO_2 selectivity reduced. During the gas flux measurement, it was observed that the top selective layer could be easily detached from the rest of the composite layers. It appeared that the adhesion between the PTMSP gutter layer and the Pebax®/PEG POSS® selective layer was relatively weak, and in turn, the exposure of a given pressure to the composite membrane severely affected the adhesion between those layers. The polyacetylenes, i.e., PTMSP, is well know with their hidrophobicity characteristic [71], meanwhile Pebax® is hydrophilic polymer [63]. Thereby, it can be understood that the PTMSP chains will inherently repulse the Pebax® copolymers. When the POSS containing PEG polar groups introduced into the Pebax® matrix, the interaction between the selective and gutter layers presumably were weakened due to the increased hydrophilicity from the PEG groups. If the selective layer is not well–adhered to the gutter layer, it creates such a ′gap′ between the selective–gutter layers. The creating ′gap′ causes the diffusion pathways longer, and thus reducing the gas separation performance of the membranes.

To overcome the adhesion issue, the composite membranes with Pebax® concentration of 0.5 wt% and different concentration of PEG POSS® were prepared. Since the concentration of the Pebax® was reduced, the selective–gutter layers adhesion was better than the previous case. The figure IV.3 showed that the SEM analyses confirmed the good adhesion.

As it was expected, the membrane selectivity would also reduce as the concentration of Pebax® was lowered to 0.5 wt%. However, it was not expected that the addition of POSS particles did not affect the CO_2 selectivity of these membranes.

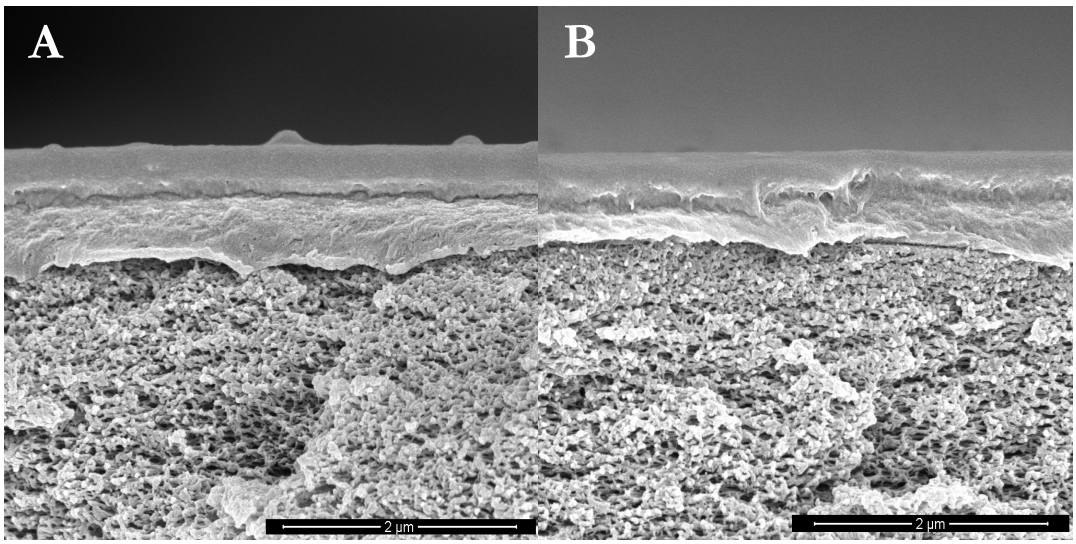


Figure IV.3: Cross–sectional morphologies of mixed matrix composite membranes prepared from Pebax 0.5 wt% with PEG POSS® content (wt%) of (a)0.1 and (b)0.5

With the highest PEG POSS® loadings, the CO_2 selectivity even was similar to the one prepared from pure Pebax® (see the control sample). Despite there was assumed that defects might be present in the selective layer, the reduced CO_2 selectivities still could not be explained when small amount of POSS particles were added into the 0.5 wt% membranes.

From the data shown above, a trend can be observed for the gas permeation rate in both of the MMCs. As the filler content was enhanced, the permeation rate decreased. In organic–inorganic hybrid system, the compatibility and adhesion between the fillers and polymer matrix significantly determine the resultant gas transport properties. If the polymers chain are so compatible with the fillers, so that the polymer chains wet the fillers and the fillers do not affect the matrix properties, the nonporous fillers will reduce the gases permeabilities [46, 72]. This might be the case when the PEG POSS® particles were added into the polymer matrix. It appeared that the particles interacted strongly with the PEO segments through hydrogen bonding. The strong interaction will cause the penetrants diffusion pathways become more tortuous, then it will simultaneously decrease the molecular transport

across the membrane, and thus resulting decreased in permeabilities. The strong particles–polymer interaction can be evidenced from the optical transparency of the hybrid membranes that have been discussed in the beginning of this discussion. It also appeared that the Maxwell model (see section IV.1.2) could be useful to predict the permeation rate in the current MMCS.

Chapter V

Conclusion

Dense and composite membranes of hybrid Pebax®/PEG POSS® were prepared in this study. The transparent dense membranes were obtained by varying the ethanol/-water mixture compositions. The addition of 1,4–dioxane to the ethanol/water mixture could effectively prevent the fillers agglomeration in the macroscopic scale. The DSC analyses further showed that the incorporation of PEG POSS® into Pebax® resulted in the increased glass transition temperature of the polymer matrix. It is suggested that the free volume available in the matrix decreased and presumably caused the alteration of Pebax® gas transport properties.

Both single layer and multi layer composite membranes were also prepared. Single layer composite membrane consisting of PAN support layer and low concentrations of pure Pebax® exhibited high gas permeation rates that were coupled with low CO_2 selectivities. It showed that the selective polymer coils could penetrate into the pore support and thus dramatically dropped the selectivity of Pebax®.

Two strategies were then investigated to prevent the polymer incursion into support layer. First approach was by filling the pores with ethanol/water mixture prior casting of the selective layer. This approach effectively increased the permeation rates of CO_2, however, it caused simultaneous loss of CO_2 selectivities. Another approach was the application of PTMSP gutter layer between the support and selective layers. Compared to the first approach, the composite membrane which was constructed with gutter layer exhibited high selectivity while keeping the permeation rate almost intact.

Finally, the multilayer composite membranes (MMCs) consisting of PAN porous

support, PTMSP gutter layer, and hybrid selective top layer were investigated. These MMCs exhibited slight increase in CO_2 selectivity due to the addition of ether oxide linkages by PEG groups from the POSS particles. Nevertheless, when the selective layer was prepared from 2 wt% of Pebax®, this top layer was poorly adhered with the gutter layer. It appeared that the addition of PEG moities enhanced the hydrophilicity of Pebax® material, so that repulsed the PTMSP chains. By reducing the Pebax® concentration to 0.5 wt%, a good adhesion could be obtained. In the same time, it also resulted in reduction of gas transport performances of MMCs. It implied that the composition and intrinsic material properties play key roles in multilayer composite membranes, and the good interplay of these factors will finally determine the resultant gas separation properties.

BIBLIOGRAPHY

[1] H. Cong, M. Radosz, B. F. Towler, and Y. Shen, "Polymer-inorganic nanocomposite membranes for gas separation," *Separation and Purification Technology*, vol. 55, pp. 281–291, 2007.

[2] V. I. Bondar, B. D. Freeman, and I. Pinnau, "Gas sorption and characterization of poly(ether-b-amide) segmented block copolymers," *Journal of Polymer Science Part B: Polymer Physics*, vol. 37, pp. 2463–2475, 1999.

[3] Hybrid-Plastics, "Peg poss® cage mixture," accessed on April, 14 2010. [Online]. Available: http://www.hybridplastics.com/products/pg1190.htm

[4] K. Takada, H. Matsuya, T. Masuda, and T. Higashimura, "Gas permeability of polyacetylenes carrying substituents," *Journal of Applied Polymer Science*, vol. 30, pp. 1605–1616, 1985.

[5] J. H. Kim, S. Y. Ha, and Y. M. Lee, "Gas permeation of poly(amide–6–b–ethylene oxide) copolymer," *Journal of Membrane Science*, vol. 190, pp. 179–193, 2001.

[6] R. W. Baker, "Future directions of membrane gas separation technology," *Industrial & Engineering Chemistry Research*, vol. 41, pp. 1393–1411, 2002.

[7] P. Bernardo, E. Drioli, and G. Golemme, "Membrane gas separation: A review/state of the art," *Industrial & Engineering Chemistry Research*, vol. 48, pp. 4638–4663, 2009.

[8] "Graphic detail: Gas exchange: CO_2 emissions 1990-2006," 2007, published online 27 June 2007 in Nature 447, 1038.

[9] R. W. Baker, "Gas separation," in *Membrane technology and applications*. John Wiley & Sons, 2004, pp. 301–353.

[10] W. J. Koros and G. K. Fleming, "Membrane–based gas separation," *Journal of Membrane Science*, vol. 83, pp. 1–80, 1993.

[11] K. Ghosal and B. D. Freeman, "Gas separation using polymer membranes: An overview," *Polymers for Advanced Technologies*, vol. 5, pp. 673–697, 1994.

[12] S. P. Nunes and K. V. Peinemann, "Gas separation with membranes," in *Membrane technology: In the chemical industry*, S. P. Nunes and K. V. Peinemann, Eds. Wiley–VCH Verlag GmbH & Co. KGaA, 2006, pp. 53–90.

[13] L. M. Robeson, "Correlation of separation factor versus permeability for polymeric membranes," *Journal of Membrane Science*, vol. 62, pp. 165–185, 1991.

[14] W. J. Koros and R. Mahajan, "Pushing the limits on possibilities for large scale gas separation: Which strategies?" *Journal of Membrane Science*, vol. 175, pp. 181–196, 2000.

[15] J. Qiu, "Nanocomposite gas separation membrane," Ph.D. dissertation, University of Hamburg, 2009.

[16] C. M. Zimmerman, A. Singh, and W. J. Koros, "Tailoring mixed matrix composite membranes for gas separations," *Journal of Membrane Science*, vol. 137, pp. 145–154, 1997.

[17] M. Kawakami, H. Iwanaga, Y. Hara, M. Iwamoto, and S. Kagawa, "Gas permeabilities of cellulose nitrate/poly(ethylene glycol) blend membranes," *Journal of Applied Polymer Science*, vol. 27, pp. 2387–2393, 1982.

[18] J. Li, K. Nagai, T. Nakagawa, and S. Wang, "Preparation of polyethyleneglycol (peg) and cellulose acetate (ca) blend membranes and their gas permeabilities," *Journal of Applied Polymer Science*, vol. 58, pp. 1455–1463, 1995.

[19] H. Lin and B. D. Freeman, "Materials selection guidelines for membranes that remove CO_2 from gas mixtures," *Journal of Molecular Structure*, vol. 739, pp. 57–74, 2005.

[20] V. I. Bondar, B. D. Freeman, and I. Pinnau, "Gas transport properties of poly(ether-b-amide) segmented block copolymers," *Journal of Polymer Science Part B: Polymer Physics*, vol. 38, pp. 2051–2062, 2000.

[21] G. Z. Li, L. C. Wang, H. L. Ni, and C. U. Pittman, "Polyhedral oligomeric silsesquioxane (poss) polymers and copolymers: A review," *Journal of Inorganic and Organometallic Polymers*, vol. 11, pp. 123–154, 2001.

[22] Y. Ichiraku, S. A. Stern, and T. Nakagawa, "An investigation of the high gas permeability of poly(1-trimethylsilyl-1-propyne)," *Journal of Membrane Science*, vol. 34, pp. 5–18, 1987.

[23] E. E. Walker, "The solvent action of organic substances on polyacrylonitrile," *Journal of Applied Chemistry*, vol. 2, pp. 470–481, 1952.

[24] H. K. Lonsdale, "The growth of membrane technology," *Journal of Membrane Science*, vol. 10, pp. 81–181, 1982.

[25] W. J. Koros and R. Chern, "Separation of gaseous mixtures using polymer membranes," in *Handbook of separation process technology*, R. W. Rousseau, Ed. John Wiley & Sons, 1987, pp. 862–953.

[26] S. Alexander Stern, "Polymers for gas separations: the next decade," *Journal of Membrane Science*, vol. 94, pp. 1–65, 1994.

[27] J. G. Wijmans and R. W. Baker, "The solution–diffusion model: a review," *Journal of Membrane Science*, vol. 107, pp. 1–21, 1995.

[28] M. Mulder, *Transport in membranes*. Dordrecht: Kluwer Academic Publisher, 1996.

[29] W. J. Koros and D. R. Paul, "Observations concerning the temperature dependence of the langmuir sorption capacity of glassy polymers," *Journal of Polymer Science: Polymer Physics Edition*, vol. 19, pp. 1655–1656, 1981.

[30] T.-S. Chung, L. Y. Jiang, Y. Li, and S. Kulprathipanja, "Mixed matrix membranes (mmms) comprising organic polymers with dispersed inorganic fillers for gas separation," *Progress in Polymer Science*, vol. 32, pp. 483–507, 2007.

[31] M. A. Aroon, A. F. Ismail, T. Matsuura, and M. M. Montazer-Rahmati, "Performance studies of mixed matrix membranes for gas separation: A review," *Separation and Purification Technology*, vol. 75, pp. 229–242, 2010.

[32] T. C. Merkel, B. D. Freeman, R. J. Spontak, Z. He, I. Pinnau, P. Meakin, and A. J. Hill, "Sorption, transport, and structural evidence for enhanced free volume in poly(4–methyl–2–pentyne)/fumed silica nanocomposite membranes," *Chemistry of Materials*, vol. 15, pp. 109–123, 2003.

[33] S. Hashemifard, A. Ismail, and T. Matsuura, "Prediction of gas permeability in mixed matrix membranes using theoretical models," *Journal of Membrane Science*, vol. 347, pp. 53–61, 2010.

[34] T. B. Lewis and L. E. Nielsen, "Dynamic mechanical properties of particulate–filled composites," *Journal of Applied Polymer Science*, vol. 14, pp. 1449–1471, 1970.

[35] R. Pal, "Permeation models for mixed matrix membranes," *Journal of Colloid and Interface Science*, vol. 317, pp. 191–198, 2008.

[36] D. Shekhawat, D. R. Luebke, and H. W. Pennline, "A review of carbon dioxide selective membranes: A topical report," National Energy Technology Laboratory of United States Department of Energy, Tech. Rep., 2003.

[37] L. S. Schadler, "Polymer–based and polymer–filled nanocomposites," in *Nanocomposite science and technology*, P. M. Ajayan, L. S. Schadler, and P. V. Braun, Eds. Wiley-VCH Verlag GmbH & Co. KGaA, 2004, pp. 77–153.

[38] A. Javaid, "Membranes for solubility–based gas separation applications," *Chemical Engineering Journal*, vol. 112, pp. 219–226, 2005.

[39] T. C. Merkel, B. D. Freeman, R. J. Spontak, Z. He, I. Pinnau, P. Meakin, and A. J. Hill, "Ultrapermeable, reverse–selective nanocomposite membranes," *Science*, vol. 296, pp. 519–522, 2002.

[40] N. P. Patel, A. C. Miller, and R. J. Spontak, "Highly CO_2–permeable and selective polymer nanocomposite membranes," *Advanced Materials*, vol. 15, pp. 729–733, 2003.

[41] W. Yave, A. Car, S. S. Funari, S. P. Nunes, and K.-V. Peinemann, "CO_2–philic polymer membrane with extremely high separation performance," *Macromolecules*, vol. 43, pp. 326–333, 2010.

[42] B. M. Novak, "Hybrid nanocomposite materials – between inorganic glasses and organic polymers," *Advanced Materials*, vol. 5, pp. 422–433, 1993.

[43] K. Kusakabe, K. Ichiki, J. ichiro Hayashi, H. Maeda, and S. Morooka, "Preparation and characterization of silica–polyimide composite membranes coated on porous tubes for co2 separation," *Journal of Membrane Science*, vol. 115, pp. 65–75, 1996.

[44] T. C. Merkel, Z. He, I. Pinnau, B. D. Freeman, P. Meakin, and A. J. Hill, "Effect of nanoparticles on gas sorption and transport in poly(1–trimethylsilyl–1–propyne)," *Macromolecules*, vol. 36, pp. 6844–6855, 2003.

[45] X. Hu, H. Cong, Y. Shen, and M. Radosz, "Nanocomposite membranes for CO_2 separations: silica/brominated poly(phenylene oxide)," *Industrial & Engineering Chemistry Research*, vol. 46, pp. 1547–1551, 2007.

[46] R. A. Zoppi, S. das Neves, and S. P. Nunes, "Hybrid films of poly(ethylene oxide–b–amide–6) containing sol–gel silicon or titanium oxide as inorganic fillers: effect of morphology and mechanical properties on gas permeability," *Polymer*, vol. 41, pp. 5461–5470, 2000.

[47] J. H. Kim and Y. M. Lee, "Gas permeation properties of poly(amide–6–b–ethylene oxide)–silica hybrid membranes," *Journal of Membrane Science*, vol. 193, pp. 209–225, 2001.

[48] D. B. Cordes, P. D. Lickiss, and F. Rataboul, "Recent developments in the chemistry of cubic polyhedral oligosilsesquioxanes," *Chemical Reviews*, vol. 110, pp. 2081–2173, 2010.

[49] Y. Li and T.-S. Chung, "Molecular–level mixed matrix membranes comprising pebax® and poss for hydrogen purification via preferential CO_2 removal," *International Journal of Hydrogen Energy*, vol. 35, pp. 10 560–10 568, 2010.

[50] N. P. Patel, J. M. Zielinski, J. Samseth, and R. J. Spontak, "Effects of pressure and nanoparticle functionality on CO_2–selective nanocomposites derived from crosslinked poly(ethylene glycol)," *Macromolecular Chemistry and Physics*, vol. 205, pp. 2409–2419, 2004.

[51] W. J. Koros and I. Pinnau, "Membrane formation for gas separation processes," in *Polymeric Gas Separation Membranes*, P. Donald R. and Y. P. Yampol'skii, Eds. CRC Press, Inc., 1994, pp. 209–272.

[52] J. M. Henis and M. K. Tripodi, "Composite hollow fiber membranes for gas separation: the resistance model approach," *Journal of Membrane Science*, vol. 8, pp. 233–246, 1981.

[53] I. Pinnau, J. G. Wijmans, I. Blume, T. Kuroda, and K. V. Peinemann, "Gas permeation through composite membranes," *Journal of Membrane Science*, vol. 37, pp. 81–88, 1988.

[54] K. A. Lundy and I. Cabasso, "Analysis and construction of multilayer composite membranes for the separation of gas mixtures," *Industrial & Engineering Chemistry Research*, vol. 28, pp. 742–756, 1989.

[55] L. H. Sperling, *Introduction to physical polymer science*, 4th ed. John Wiley & Sons, 2006.

[56] S. Wiederhorn, R. Fields, S. Low, G.-W. Bahng, A. Wehrstedt, and et al., "Mechanical properties," in *Springer handbook of materials measurement methods*, H. Czichos, T. Saito, and L. Smith, Eds. Springer Science+Business Media, 2006, pp. 283–397.

[57] J. Mu, Y. Liu, and S. Zheng, "Inorganic–organic interpenetrating polymer networks involving polyhedral oligomeric silsesquioxane and poly(ethylene oxide)," *Polymer*, vol. 48, pp. 1176–1184, 2007.

[58] K. Madhavan and B. Reddy, "Structure–gas transport property relationships of poly(dimethylsiloxane–urethane) nanocomposite membranes," *Journal of Membrane Science*, vol. 342, pp. 291–299, 2009.

[59] D. v. Krevelen, *Properties of polymers*, fourth, completely revised edition. ed., K. t. Nijenhuis, Ed. Elsevier, 2009.

[60] Hybrid-Plastics, *POSS® user's guide: A guide to developing new products with POSS®*, version 2.06 ed., 2011, downloaded from www.hybridplastics.com/pdf/user-v2.06.pdf.

[61] R. Mahajan and W. J. Koros, "Factors controlling successful formation of mixed–matrix gas separation materials," *Industrial & Engineering Chemistry Research*, vol. 39, pp. 2692–2696, 2000.

[62] A. F. M. Barton, *Handbook of solubility parameters and other cohesion parameters*. Boca Raton, FL: CRC Press, 1983.

[63] A. Car, C. Stropnik, W. Yave, and K.-V. Peinemann, "Peg modified poly(amide–b–ethylene oxide) membranes for CO_2 separation," *Journal of Membrane Science*, vol. 307, pp. 88–95, 2008.

[64] E. Markovic, M. Ginic-Markovic, S. Clarke, J. Matisons, M. Hussain, and G. P. Simon, "Poly(ethylene glycol)–octafunctionalized polyhedral oligomeric silsesquioxane:synthesis and thermal analysis," *Macromolecules*, vol. 40, pp. 2694–2701, 2007.

[65] I. Blume and I. Pinnau, "Composite membrane, method of preparation and use," US Patent Patent 4 963 165, October, 1990.

[66] S. C. Williams, B. Bikson, J. K. Nelson, and R. D. Burchesky, "Method for preparing composite membranes for enhanced gas separation," US Patent Patent 4 840 819, June, 1989.

[67] J. Peter and K.-V. Peinemann, "Multilayer composite membranes for gas separation based on crosslinked ptmsp gutter layer and partially crosslinked matrimid® 5218 selective layer," *Journal of Membrane Science*, vol. 340, pp. 62–72, 2009.

[68] L. Robeson, W. Burgoyne, M. Langsam, A. Savoca, and C. Tien, "High performance polymers for membrane separation," *Polymer*, vol. 35, pp. 4970–4978, 1994.

[69] R. Srinivasan, S. Auvil, and P. Burban, "Elucidating the mechanism(s) of gas transport in poly[1–(trimethylsilyl)–1–propyne] (ptmsp) membranes," *Journal of Membrane Science*, vol. 86, pp. 67–86, 1994.

[70] T.-S. Chung, R. E. Kafchinski, M. Spak, B. Bembry-Ross, and G. C. Wensley, "High performance pan composite membranes," US Patent Patent 5 324 430, June, 1994.

[71] K. Nagai, T. Masuda, T. Nakagawa, B. D. Freeman, and I. Pinnau, "Poly[1-(trimethylsilyl)-1-propyne] and related polymers: Synthesis, properties and functions," *Progress in Polymer Science*, vol. 26, pp. 721–798, 2001.

[72] B. D. Freeman, "Novel nanocomposite membrane structures for H_2 separations," in *DOE University Coal Research Contractors' Meeting*. National Energy Technology Laboratory, 2003. [Online]. Available: http://www.netl.doe.gov/publications/proceedings/03/ucr-hbcu/Freeman.pdf